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SYNTHESIS AND THERMAL PROPERTIES OF NOVEL MALEONITRILES

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ABSTRACT

In this study, the synthesis and thermal properties of two novel maleonitriles bearing 8-membered heterocyclic derivatives is described first time. New maleonitriles, benzo-(1,2-bis-methylthio)maleonitrile and [Benzo-15-crown-5]-(4,5-bis-methylthio)maleonitrile have been prepared by the reaction of different alkyl halides such as 1,2-bis(brommethyl)benzene and 4,5-bis-(brommethyl)[benzo-15-crown-5] with dithiomaleonitrile disodium salt. Both compounds are characterized by IR, Mass, NMR spectroscopy as well as elemental analysis.

Keywords: Macrocycle, maleonitrile, crown ethers, thermal properties.

YENİ MALEONİTRİLLERİN SENTEZİ VE TERMAL ÖZELLİKLERİ

ÖZ

Bu çalışmada ilk kez, iki yeni sekiz üyeli heterosiklik maleonitril bileşiğinin sentezi ve termal özellikleri çalışılmıştır. Benzo-(1,2-bis-metiltiyo)maleonitril ve [Benzo-15-taç eter-5]-(4,5-bis-metiltiyo)maleonitril bileşikleri 1,2-bis(bromometil)benzen ve 4,5-bis-(bromometil)[benzo-15-taç eter-5] gibi farklı alkil halojen bileşikleri ve ditiomaleonitril disodyum reaksiyonu sonucu elde edilmiştir. Her iki bileşik FT-IR, Kütle, ^{1}H NMR ve elementel analiz yöntemleri ile karakterize edilmiştir.

Anahtar Sözcükler: Makrosiklik bileşikler, maleonitril, taç eterler, termal özellikler.

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1. INTRODUCTION

Maleonitrile is an important reagent in synthetic chemistry, both in the laboratory and in industry. Numerous Diels-Alder [1-4] reactions using maleonitrile as a reagent have appeared in the literature. Maleonitrile is useful for making polymers [5,6]. It is also used widely in the laboratory [7-/13] in areas such as preparing organometallic compounds [10-12] and magnetic and conducting polymers [13]. Interest in synthesizing new derivatives of maleonitrile stems from their extensive use as precursors to porphyrazines. The possibility to functionalize porphyrazines on the periphery can be achieved by addition of different groups to these unsaturated 1,2-dinitrile derivatives. Among the tetrapyrrol compounds, porphyrazines have been receiving more frequent attention recently, mainly due to the utility of these species in molecular

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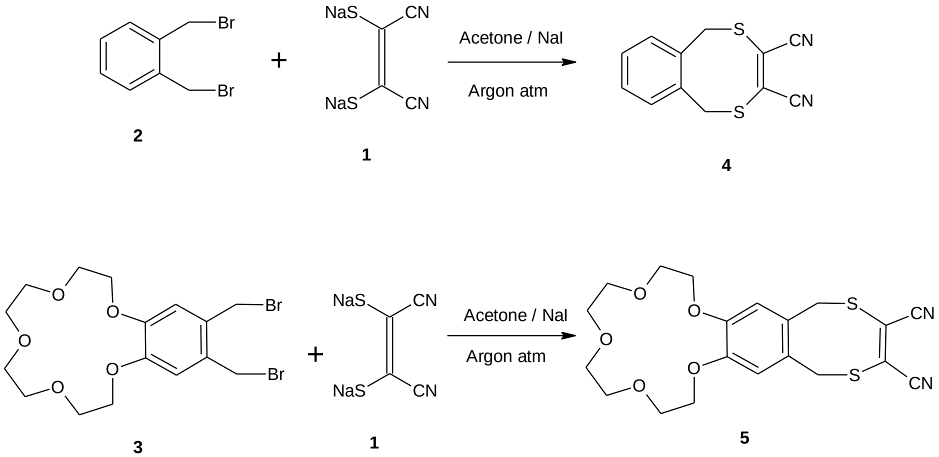
materials [14,15]. It has been already shown that incorporation of crown ethers to other tetrapyrrol derivatives, namely phthalocyanines and porphyrins, result in products attractive as potential sensors for metal ions and as building blocks in supramolecular assemblies [16,17]. Our previous studies have been heavily engaged with the preparation of derivatives with additional functionalities such as, 3-Methylbutyl-[18], 3-Phenylpropyl-[19], dithiomaleonitrile. Recently, heterocyclic products obtained by the addition reaction of disodium salt of maleonitrile to unsaturated reagents have been converted into porphyrazine derivatives [20]. Crown ether derivatives with ethereal or anionic groups on the periphery of the macrocycles have been developed, in order to increase metal selectivity and complex stability in analytical and separation methods as well as in biological membranes [21–27].

In the present work, we report the synthesis of a 8-membered heterocyclic product (**4**) and its carrying crown ether derivative (**5**) as potential starting materials for porphyrazines and to compare thermal properties [28] (Scheme 1).



Scheme 1. Synthetic route of novel maleonitriles **4** and **5**.

2. EXPERIMENTAL

2.1. Materials

All of the reagents were purchased from Merck. Column chromatography was performed on silica gel 60 (0.04–0.063mm). dithiomaleonitrile disodium salt (**1**) 1,2-bis(brommethyl)benzene (**2**) and 4,5-bis-(brommethyl)[benzo-15-crown-5] (**3**) were prepared, purified and characterized according to literature procedures [29,31] respectively.

2.2. Equipment

FT-IR spectra (KBr pellets) were recorded on a Perkin Elmer Spectrum One Spectrometer. The mass spectra were acquired on a FAB-MS: Ultimate Fourier Transform and Varian 711 and GC-MS: Agilent Technologies 6890 N Network GC System, Agilent 5973 inert Mass selective Detector. ^1H NMR spectra were recorded in $CDCl_3$ and $DMSOd_6$ solutions on a Varian Unity Inova 300 MHz spectrometer. Elemental analyses were obtained with a Thermo flash EA 1112 Series. Thermogravimetric analysis (TGA) is a thermoanalytical method, in which the weight variation of a sample heated at a constant rate is measured continuously. From the temperature derivative of these spectra, differential thermogravimetric analysis (DTG), it is possible to obtain peak temperatures associated with a maximum rate of weight loss. Thermogravimetric analysis (TGA) was done using a TA SDT Q600. Nitrogen gas was set to run at 20 ml/min to provide a controlled combustion environment. TGA was carried out in the temperature range of 30–1500 ºC.

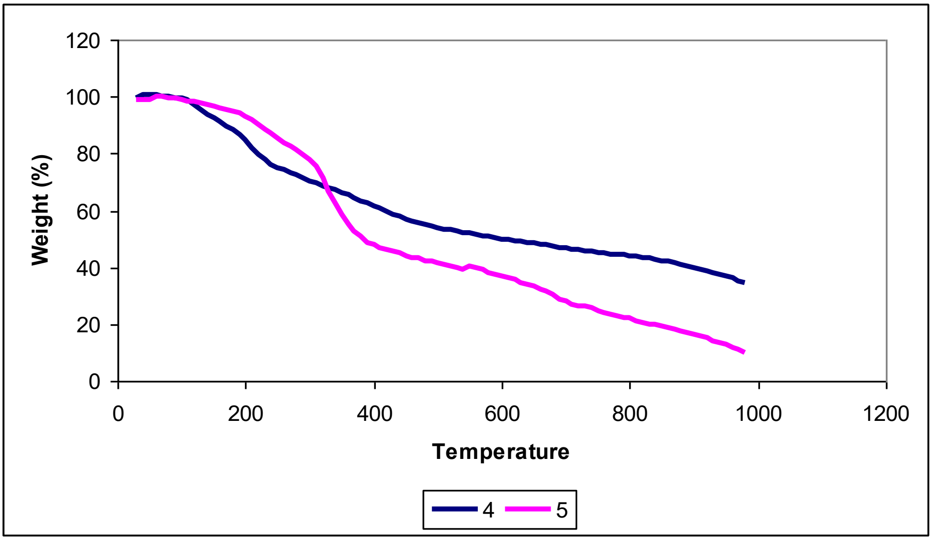


Figure 1. Spectra of TGA maleonitriles **4** and **5**

2.3 Synthesis

2.2. Preparation of benzo-(1,2-bis-methylthio)maleonitrile (4)

Dithiomaleonitrile disodium salt (**1**) (2.70 g, 10.00 mmol) was mixed with 1,2-bis(brommethyl)benzene (**2**) (1.86 g, 10.00 mmol) and NaI (0.60 g, 40 mmol) in 100.00 mL of acetone and refluxed at 60 °C for about 24 h. Then acetone was evaporated and the remaining yellow solid was treated with $CHCl_3$ to remove insoluble salts by decantation. The $CHCl_3$ phase was treated several times with anhydrous Na_2SO_4. Finally the crude product obtained by evaporation of the solvent was chromatographed on a silica column (Eluent: $CHCl_3$). The final product is soluble in chloroform, acetone, dichloromethane and THF. Yield: 0.44 g, 20 %. Calc. for $C_{12}H_8N_2S_2$ (%): C, 58.99; H, 3.30; N, 11.47; S, 26.25. Found (%): C, 59.10; H, 3.22; N, 11.41; S, 26.32. **IR** (KBr), ν/cm^{-1}: 3025 (Ar-CH), 2912, 2872 ν (Alph.-CH), 2211 ν (C≡N), 1165 ν (C-S-C). **^{1}H NMR** ($CDCl_3$, 500 MHz,): δ = 7.16 (m, 4H, Ar-H); δ = 4.48 (s, 4H, S-H). **MS (GC-MS)** m/z: Calcd: 244.3, Found: 244.01.

2.3. Preparation of [Benzo-15-crown-5]-(4,5-bis-methylthio)maleonitrile (5)

Dithiomaleonitrile disodium salt (**1**) (2.70 g, 10.00 mmol) was mixed with 4,5-bis-(brommethyl)[benzo-15-crown-5] (**4**) (1.86 g, 10.00 mmol) and NaI (0.60 g, 40 mmol) in 100.00 mL of acetone and refluxed at 60°C for about 24 h under argon atmosphere. After reaction time acetone was evaporated and the remaining yellow solid was treated with $CHCl_3$ to remove insoluble salts by decantation. The $CHCl_3$ phase was treated several times with anhydrous

Na_2SO_4. Finally the crude product obtained by evaporation of the solvent was washed with water, hexane and diethyl ether, respectively. The final product is soluble in chloroform, acetone, dichloromethane and THF. Yield: 0.50 g, 22 %. Calc. for $C_{12}H_8N_2S_2$ (%):C, 55.28; H, 5.10; N, 6.45; S, 14.76. Found (%): C, 55.47; H, 5.01; N, 6.39; S, 14.67. **IR** (KBr), ν/cm^{-1}: 3062, 3041 (Ar-CH), 2941, 2879 ν (Alph.-CH), 2204 ν (C≡N), 1278 (C-O-C$_{Ar}$), 1132, 1030 ν (C-O-C$_{Alph.}$), 1175 ν (C-S-C). **^{1}H NMR** (DMSO-d$_6$, 300 MHz,): δ = 7.21 (m, 2H, Ar-H); δ = 4.42 (s, 4H, S-H); δ = 4.01-3.20 (m, 16H, O-CH$_2$-O-CH$_2$). **MS (FAB-MS)** m/z: Calcd: 484.52, Found; 434.24 [M]$^+$

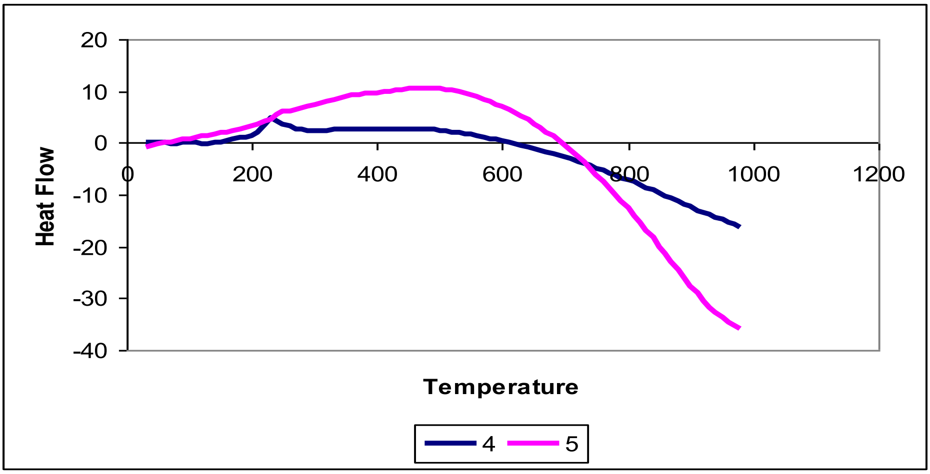


Figure 2. Spectra of DSC maleonitriles **4** and **5**

3. RESULTS AND DISCUSSION

3.1. Synthesis and characterization

Both new maleonitriles (**4** and **5**) were purified by column chromatography (for **4**) and washed with different solvents (for **5**) .They were obtained in a moderate yield (20% for **4** and 21% for **5**) and were characterized by elemental analysis together with the spectral data (^{1}H NMR, FTIR, mass spectroscopy). The characterization data of the new compounds are consistent with the assigned formula as shown in the experimental section. The alkylation process was accomplished with 1,2-bis(brommethyl)benzene (for **4**) and 4,5-bis-(brommethyl)[benzo-15-crown-5] (for **5**) in acetone. The cyclization reaction between **1** and **2** or **3** gave 8-membered dithiaheterocycles (**4** and **5**). The alkylated dithiomaleonitrile is a very suitable starting material for porphyrazine derivatives. These compounds are soluble in chloroform, acetone, DMSO, DMF and THF. In the IR spectrum of these compounds, characteristic C–H stretching vibration belonging to CH$_2$ groups occurs at 2912 and 2872 cm^{-1} for **4** and 2941 and 2879 cm^{-1} for **5** respectively. The characteristic vibrations corresponding to CN were observed at 2211 cm^{-1} for **4** and at 2204 cm^{-1} for **5**. The thio ethers (C-S-C) peaks for **4** and **5** were observed at 1165cm^{-1} and at 1175 cm^{-1}**,** respectively. Compound **5** also showed characteristic vibrations belong to ether groups (C-O-C$_{Ar}$) at 1278 cm^{-1} and (C-O-C$_{Alph}$) 1132 cm^{-1} respectively. Aromatic C-H peaks occurred at 3025 cm^{-1} and 3041 cm^{-1} for the maleoalonitriles (**4** and **5**).

The ^{1}H NMR spectrums of **4** in CDCl$_3$ and **5** in DMSO-d$_6$ are compatible with other results. In the ^{1}H NMR spectrum of the compound **4**, chemical shifts as signable to -SCH$_2$ and benzene groups are recorded at 4.48 ppm and 7.16 ppm respectively. The ^{1}H NMR spectrum of the compound **5** in DMSO-d_6 confirmed the proposed structure. The assignments of the protons are highly complicated in the regions 4.42 ppm, 3.20–4.01 ppm and 7.21 ppm, where the signals are due to the protons of SCH_2, ethylenic chains of the crown ether moiety and aromatic group. In the ^{1}H NMR spectrums, there was only one chemical shift for SCH_2 at about 4.40 ppm due to the symmetrical structure of the molecules **4** and **5**.

In the mass spectra, the molecular ion peaks of the compounds **4** and **5** appeared at m/z 244.01 $[M]^+$ and 434.24 $[M]^+$ in the GC/MS and FAB-MS spectra respectively.

Elemental analyses of the maleonitriles **4** and **5** show good agreements with the proposed structures, as shown in Scheme 1.

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 [28].

3.2. Thermal properties

Thermal properties of the maleonitriles (**4, 5**) were investigated by TGA-DSC. Thermo gravimetric (TGA) and differential scanning calorimetric (DSC) curves for the maleonitriles are presented in Fig. 1 and Fig. 2. It can clearly be seen that the TGA curves of the two compounds do not show any mass losses up to 133 °C, which indicates the thermal stability of these maleonitriles and that no water molecules were incorporated in the samples. The TGA curves indicate that the maleonitriles **4** and **5** start to decompose at 155 and 133 °C, respectively. Comparison of the Td (decomposition temperatures) of the maleonitriles shows that **4** decomposes later than **5**.

None of the maleonitriles showed a melting process and decomposed directly from the solid state, as detected by exothermic peaks in the DSC trace. As the temperature is increased, the TGA curves of **4** and **5** exhibit sharp decompositions at about 238 and 218 °C, respectively. These data indicate that all of the synthesized maleonitriles have good and thermal stability (Table 1).

Table 1. Thermal properties of maleonitriles

Maleonitriles	Initial decomposition temperature in °C	Main decomposition temperature in °C
4	155	238
5	133	218

4. CONCLUSION

In the presented work, the synthesis of novel 8-membered dithiaheterocycles maleonitrile compounds were described and these new complexes were characterized by elemental analysis, FT-IR, ^{1}H-NMR spectroscopy and mass spectra. Also, thermal properties of the maleonitriles were examined by thermogravimetric analysis. Compound **4** indicated the more stabile than compound **5**. The solubility in organic solvents increased, because of introducing of crown ether group into maleonitrile. So, good solubility of maleonitrile in organic solvents is occurring important for technological materials such as sensors for metal ions and converts to porphyrazines.

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