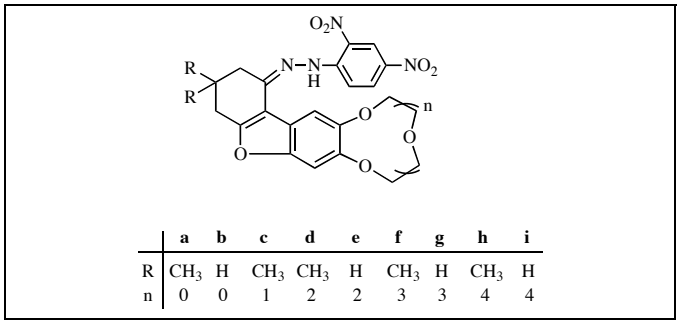
Saziye Abdurrahmanoglu and Mustafa Bulut*

University of Marmara, Department of Chemistry , 34722, Kadikoy-İstanbul, Turkey
sabdur@marmara.edu.tr, mbulut@marmara.edu.tr

Received February 9, 2006



	a	b	c	d	e	f	g	h	i
R	CH_3	H	CH_3	CH_3	H	CH_3	H	CH_3	H
n	0	0	1	2	2	3	3	4	4

We dedicate this work to a distinguished organic chemist, Çakıl ERK, who died in the summer of 2005.

The *o*-dihydroxy- (**2a-b**), dimethoxy (**3a**-**b**), ethylendioxy- (**4a**-**b**) and macrocyclic polyethers (**4c-i**) are the initial compounds while the 2,4-dinitrophenylhydrazone compounds (**5a-d**, **6a-i**) represent new derivatives. Novel hydrazone compounds were synthesized from the corresponding cyclic ketones (**4a-i**) and 2,4-dinitrophenylhydrazine in H_2SO_4/EtOH/H_2O solution at room temperature for 1 h. The structures of obtained hydrazone compounds were confirmed by ^{1}H-NMR, ^{13}C-NMR, EI-MS, IR spectra and elemental analysis.

J. Heterocyclic Chem., **44**, 205 (2007).

INTRODUCTION

Quite a number of crown ethers have been prepared since the initial synthesis by Peterson [1]. Crown ethers or cryptands are known as selective ligands for various alkaline or alkaline earth metal ions and some of the cationic metal complexes are readily extractable from the aqueous into an organic phase. The selectivity principally depends on the cavity size within the ligand molecule [2-5]. Chromogenic complexing reagents that show a distinct colour change on interaction with alkaline metal ions are practically unknown [6]. Most recently we prepared *o*-dihydroxy keto and ester compounds in good yields for obtaining their macrocyclic ether derivatives [7-10].

The present work deals with the preparation and elucidation of novel crown ethers bearing 2,4-dinitrophenylhydrazone moieties. The introduced hydrazone derivatives of crown ethers are new and can be used in purifying and characterizing the parent ketones. Initial compounds (**2a**, **2b**) and their [1,4,7,10]-tetraoxacyclododecylene (**4d-e**), [1,4,7,10,13]-pentaoxacyclododecylene (**4f-g**) and [1,4,7,10,13,16]-pentaoxacyclododecylene (**4h-i**) derivatives were synthesized according to literature [7,8]. In this study, 6,7-dimethoxy-3,3-dimethyl-3,4-dihydro-2*H*-dibenzofuran-1-one (**3a**), 6,7-dimethoxy-3,4-dihydro-2*H*-dibenzofuran-1-one (**3b**), 6,7-(ethylenedioxy)-3,3-dimethyl-3,4-dihydro-*2H*-dibenzofuran-1-one (**4a**), 6,7-(ethylendioxy)-3,4-dihydro-2*H*-dibenzofuran-1-one (**4b**), 6,7-(1,4,7-trioxacyclo-nonan)-3,3-dimethyl-3,4-dihydro-2*H*-dibenzo- furan-1-one (**4c**) were synthesized and then all these compounds were reacted with 2,4-dinitro- phenylhydrazine in ethanol to obtained new hydrazone derivatives (**5a-d**, **6a-i**). These original hydrazone derivatives are easily soluble in aprotic solvents.

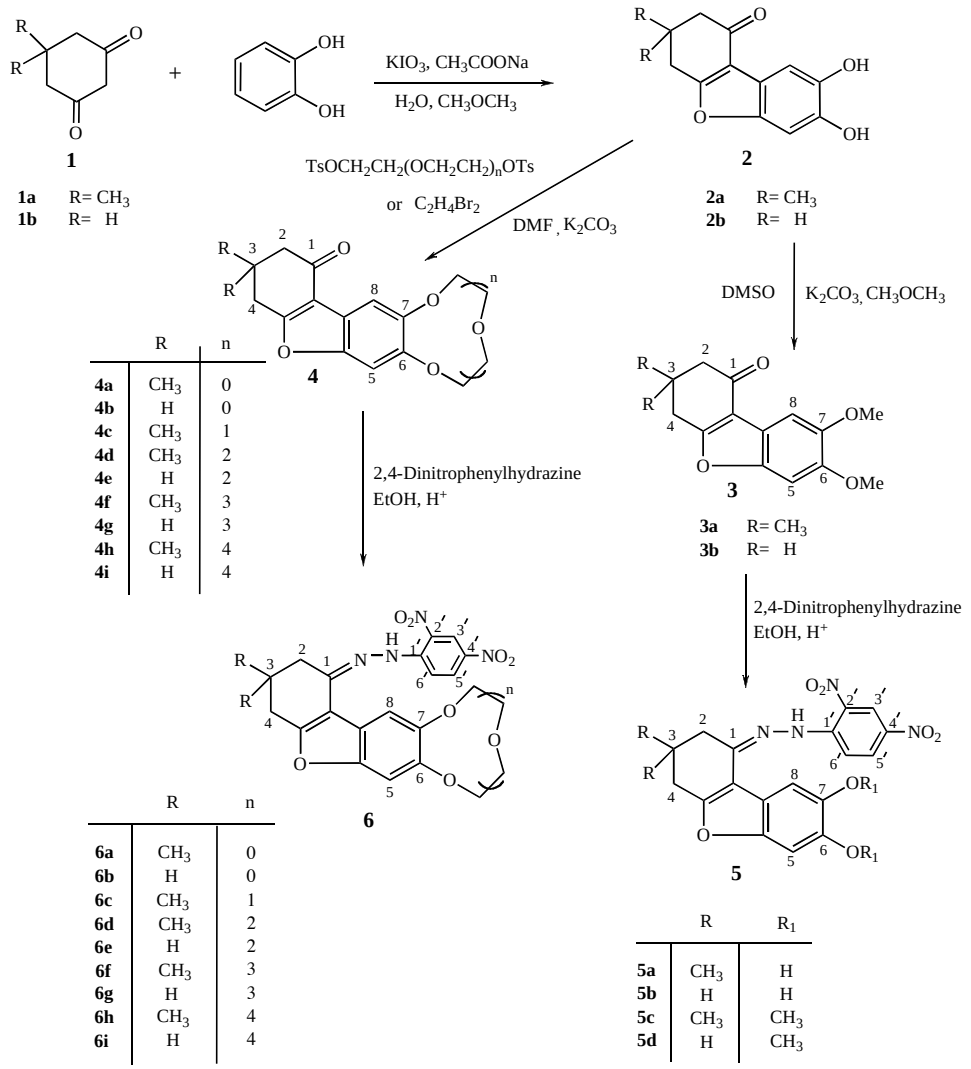
RESULTS AND DISCUSSION

Compounds **2a-b** were reacted with dimethyl sulphate in acetone in the presence of potassium cabonate to obtained **3a** and **3b**, respectively. The preparation of **4a-b** was performed by the reaction of **2a** and **2b** with 1,2-dibromoethane in DMF/K_2CO_3. 6,7-(1,4,7-trioxacyclo-nonan)-3,3-dimethyl-3,4-dihydro-2*H*-dibenzofuran-1-one (**4c**) was synthesized using diethylene glycol dittosylate in DMF/K_2CO_3. All these compounds were purified by column chromotography (silica gel) with chloroform.

Novel hydrazone derivatives **5a-d**, **6a-i** were prepared by the reaction of obtained compounds **2a-b**, **3a-b**, **4a-i** with 2,4-dinitrophenylhydrazine and the crude products were purified by crystallization with ethanol. The structures of all synthesized compounds were identified by elemental analysis, IR, ^{1}H-NMR, ^{13}C-NMR and mass spectrometry. These compounds are stable to acidic hydrolysis but readily hydrolized with titanium trichloride at neutral pH.

IR spectra of **2a** and **2b** showed hydroxyl bands around 3480 cm^{-1} this band disappeared in the spectra of **3a** and

Scheme I



3b. Two absorption bands at 2978-2850 cm^{-1} indicated the presence of C-H stretching frequency for all synthesized compounds. The characteristic absorption band of the cabonyl group at 1676 cm^{-1} for **3a**, **3b**, **4a-i** indicated the presence of ketones; the C-O-C ether chain was characterized by the absorption band at 1300-1040 cm^{-1}. The stretching peaks at around 3310 cm^{-1}, 1625 cm^{-1} and 1523-1344 cm^{-1} showed the structure of N-H, C=N and Ar-NO_2, respectively for all new hydrazone compounds.

In the ^{1}H-NMR analysis of **3a** and **5a**, which were taken in d-chloroform, six methyl protons appeared as singlet at δ 1.24 ppm and δ 1.15 ppm, respectively. In the spectra of **3a** and **3b**, OCH_3 protons were found at δ 3.97-3.93 ppm as singlets. The aliphatic protons, –CH_2-O, of crown ethers **6c-i** were shown as triplets at δ 3.67-4.31 ppm. The integration showed the presence of appropriate number of protons. The characteristic N-*H* signal at δ 11.45 ppm and aromatic signals for each compounds confirmed the structure. In high field of the spectra of dibenzofuran-1-one derivatives **2b**, **3b**, **4b**, **4e**, **4g**, **4i**, **5b**, **5d**, **6b**, **6e**, **6g**, **6i** were three groups of signals, one triplet at δ 2.52-3.01 ppm (H-4, J=6.5 Hz), one triplet at δ 2.40-2.83 ppm (H-2, J=6.5 Hz) and one quintet at δ 2.16-2.30 ppm (H-3, J=6.5 Hz).

In the ^{1}H-NMR spectra of **6f**, signals at δ 7.04 ppm (s, H-5), at δ 7.57 ppm (s, H-8), at δ 8.04 (d, H-6′, J=9.5 Hz), at δ 8.39 ppm (dd, H-5′, J=2.5 Hz) and at 9.16 ppm (d, H-3′, J=2.5 Hz) were attributed to aromatic protons. The ^{13}C-NMR spectra and mass spectra also confirmed the structure of **6f**.

EXPERIMENTAL

The starting chemicals used were of reagent grade. Melting points were obtained on a Gallenkamp apparatus. Elemental analyses were performed on a LECO CHNS 92 instrument. ^{1}H-NMR and ^{13}C-NMR spectra were determined with a Brucker

DPX-400, 400 MHz High Performance Digital FT-NMR spectrometer. IR spectra were recorded as KBr disks in the range of 400-4000 cm^{-1} on a Schimadzu FTIR-8300 spectrometer. High resolution EI-MS was obtained with Fision Instrument, model VG-ZABSPEC.

General Procedure for the Sysnthesis of Initial Compounds 2a, **2b** and **4a**, **4b**. 6,7-Dihydroxy-3,3-dimethyl-3,4-dihydro-2*H*-dibenzopyran-1-one (**2a**), 6,7-dihydroxy-3,4-dihydro-2*H*-dibenzopyran-1-one (**2b**) were obtained in good yields through the reaction of cyclohexane-1,3-dione (**1a**) and 5,5-dimethylcyclohexane-1,3-dione (**1b**) with catechol in the presence of an equivalent amount of $KIO_3/CH_3COONa/H_2O/CH_3COCH_3$, respectively [11,12].

The typical procedure for cyclization reaction leading to the ether derivatives of **2a**, **2b** is as fallows. A mixture of **2a-b** (5 mmol), 1,2-dibromoethylene or ditosylate of di-, tri-, tetra-, or pentaethylene glycols (5 mmol) and potassium carbonate (10 mmol) was dissolved in dimethylformamide (60 mL) in a 250 mL reaction flask. The mixture was heated for 40 h at 70-80°C. The solvent was evaporated *in vacuo*. Water was added to the residue and the mixture was extracted with chloroform (4x30 mL). The combined organic extracts were washed with water then dried on calcium chloride. The solution evaporated and the crude product was purified by column chromotography (silica gel 60) with chloroform.

6,7-Dimethoxy-3,3-dimethyl-3,4-dihydro-2*H*-dibenzofuran-1-one (**3a**). 6,7-Dihydroxy-3,3-dimethyl-3,4-dihydro-2*H*-dibenzofuran-1-one (**2a**) (1 g, 4.1 mmol) was dissolved in acetone (100 ml). Potassium carbonate (3.36 g, 24.4 mmol) and dimethylsulphate (3.07 g, 24.4 mmol) were added to that solution. This mixture was heated for 30 h at 65°C with stirring. Then water was added for hydrolization. Solvent was evaporated under reduced pressure and solution was extracted by chloroform (4x30 ml). Organic phase was dried on magnesium sulphate, filtered and solvent was evaporated. The product was purified by column chromotography (silica gel 60) with chloroform. Yield 0.37 g (36%,) mp. 111°C; ir (KBr) ν cm^{-1}: 2978, 2825 (C-H), 1676 (C=O), 1247, 1040 (C-O); ^{1}H-NMR (400MHz/$CDCl_3$) δ: 1.24 (s, 6H, $2CH_3$), 2.47 (s, 2H, H-2), 2.88 (s, 2H, H-4), 3.93 (s, 3H, OCH_3), 3.97 (s, 3H, OCH_3), 7.04 (s, 1H, H-5), 7.50 (s, 1H, H-8). *Anal*. Calcd. for $C_{16}H_{18}O_4$ (%): C 70.07; H 6.61. Found (%): C 69.81; H 6.65.

6,7-Dimethoxy-3,4-dihydro-2*H*-dibenzofuran-1-one (**3b**). To a solution of 6,7-dihydroxy-3,4-dihydro-2*H*-dibenzofuran-1-one (**2b**) (0.35 g, 1.6 mmol) in acetone (25 ml), potassium carbonate (1.34 g, 9.74 mmoles) and dimethylsulphate (1.23 g, 9.7 mmol) were added. This mixture was stirred for 30 h at 65°C. Then water was added for hydrolysis and solvent was evaporated under reduced pressure. The solution was extracted by chloroform (3x25 ml). Organic phase was dried with magnesium sulphate, filtered and solvent was evaporated. The product was purified by column chromotography (silica gel) with chloroform. Yield 0.22g (62%), mp. 164°C; ir (KBr) ν cm^{-1}: 2978, 2825 (C-H), 1676 (C=O), 1247, 1040 (C-O); ^{1}H-NMR (400MHz/ $CDCl_3$) δ: 2.27 (q, 2H, H-3, *J*=6.5 Hz), 2.83 (t, 2H, H-2, J=6.5 Hz), 3.01 (t, 2H, H-4, J=6.5 Hz), 3.94 (s, 3H, OCH_3), 3.97 (s, 3H, OCH_3), 7.05 (s, 1H, H-5), 7.52 (s, 1H, H-8). *Anal*. Calcd. for $C_{14}H_{14}O_4$ (%): C 68.29; H 5.69. Found (%): C 68.01; H 5.75.

6,7-(1,4,7-Trioxacyclononan)-3,3-dimethyl-3,4-dihydro-2*H*-dibenzofuran-1-one (**4c**). 6,7-Dihydroxy-3,3-dimethyl-3,4-dihydro-2*H*-dibenzofuran-1-one (**2a**) (0.50 g, 2.0 mmol) and diethyleneglycol ditosylate (0.836 g, 2.0 mmol) were dissolved in dimethyl formamide (50 ml). Potassium carbonate (0.16 g, 4.1 mmol) was added to this solution and this mixture was heated for 35 h at 75°C. Organic phase was dried on magnesium sulphate and filtered. Solvent was evaporated under reduced pressure and the solution was extracted by chloroform. The product was purified by column chromotography (silica gel) with chloroform. Yield 0.14 g (22%), mp 73°C; ir (KBr) ν cm^{-1}: 2978, 2825 (C-H), 1676 (C=O), 1300, 1200 (C-O); ^{1}H-NMR (400MHz/$CDCl_3$) δ: 1.15 (s, 6H, $2CH_3$), 2.41 (s, 2H, H-2), 2.82 (s, 2H, H-4), 3.87-4.30 (d, CH_2), 7.09 (s, 1H, H-5), 7.62 (s, 1H, H-8). ^{13}C-NMR ($CDCl_3$/TMS) δ: 30.80, 37.22, 39.75, 54.11, 74.77, 106.90, 116.58, 117.27, 121.15, 129.92, 131.81, 152.38, 152.61, 153.11, 172.30. *Anal*. Calcd. for $C_{18}H_{20}O_5$ (%): C 68.35; H 6.33. Found (%): C 68.23; H 6.38.

General Procedure for the Synthesis of 2,4-Dinitrophenylhidrazone Derivatives. A hot solution of 2,4-dinitrophenylhydrazine (2.0 mmol) in H_2SO_4 (2 ml), water (2 ml) and ethanol (10 ml) was added to a solution of *o*-dihyroxy compound **2a**, **2b**, **3a**, **3b** and crown ethers (**4a-i**) (2.02 mmoles) in ethanol (20% v/v) respectively and the mixture was stirred for 1 h. The dark red precipitate was collected by filtration, washed with water and dried with magnesium sulphate. Then the new product was recrystallized from ethanol.

6,7-Dihydroxy-3,3-dimethyl-3,4-dihydro-2*H*-dibenzofuran-1-(2,4-dinitrophenylhydrazone) (**5a**). Compound **2a** (0.46 g, 2.0 mmol), 2,4-dinitrophenylhydrazine (0.40 g, 2.0 mmol) reacted in ethanol as described above to afford **5a**. Yield 0.64 g (74%), mp >320°C; ir (KBr) ν cm^{-1}: 3478 (OH), 3310 (NH), 2978, 2825 (C-H), 1625 (C=N), 1523-1344 (Ar-NO_2); ^{1}H-NMR (400MHz/$CDCl_3$) δ: 1.15 (s, 6H, $2CH_3$), 2.52 (s, 2H, H-2), 2.71 (s, 2H, H-4), 3.62 (s, 2H, OH), 6.98 (s, 1H, H-5), 7.45 (s, 1H, H-8), 8.04 (d, 1H, H-6′, J=8.5 Hz), 8.44 (dd, 1H, H-5′, J=8.5 and 2.5 Hz), 8.97 (d, 1H, H-3′, J=2.5 Hz), 11.20 (s, 1H, N*H*); ^{13}C-NMR ($CDCl_3$/TMS) δ: 30.15, 35.39, 38.13, 39.20, 1000.24, 108.23, 113.45, 116.69, 117.56, 124.94, 131.10, 131.77, 138.59, 145.07, 145.86, 146.141, 150.34, 153.40, 162.11. *Anal*. Calcd. for $C_{20}H_{18}O_7N_4$ (%): C 56.28; H 4.25; N 13.14; Found (%): C 56.45; H 4.10; N 12.96

6,7-Dihydroxy-3,4-dihydro-*2H*-dibenzofuran-1-(2,4-dinitrophenylhydrazone) (**5b**). Compound **2b** (0.20 g, 0.9 mmol), 2,4-dinitrophenylhydrazine (0.18 g, 0.9 mmol) reacted in ethanol as described above to afford **5b**. Yield 7 mg (20.8%); mp 226°C; ir (KBr) ν cm^{-1}: 3478 (OH), 3310 (NH), 1625 (C=N), 1523-1344 (Ar-NO_2); ^{1}H-NMR (400MHz/$CDCl_3$) δ: 2.16 (q, 2H, H-3, J=6 Hz), 2.74 (t, 2H, H-2, J=6 Hz), 2.88 (t, 2H, H-4, J=6 Hz), 6.92 (s, 1H, H-5), 7.60 (s, 1H, H-8), 8.12 (d, 1H, H-6′, J=9.5 Hz), 8.35 (dd, 1H, H-5′, J=9.5 and 2.5 Hz), 9.02 (d, 1H, H-3′, J=2.5 Hz), 11.33 (s, -N*H*). *Anal*. Calcd. for $C_{18}H_{14}O_7N_4$ %: C, 75.43; H, 4.92; N, 19.56; Found (%): C, 75.20; H, 4.85; N, 19.75.

6,7-Dimethoxy-3,3-dimethyl-3,4-dihydro-*2H*-dibenzofuran-1-(2,4-dinit- rophenylhydrazone) (**5c**). Compound **3a** (0.45 g, 1.5 mmol), 2,4-dinitrophenylhydrazine (0.30 g, 1.5 mmol) reacted in ethanol as described above to afford **5c**. Yield 0.35 g (51%), mp 243°C; ir (KBr) ν cm^{-1}: 3310 (NH), 2978, 2850 (C-H), 1625 (C=N), 1573 (C=C), 1523 (Ar-NO_2), 1300-1200 (Ar-O), 1075-1040 (CH_2-O); ^{1}H-NMR (400MHz/ $CDCl_3$) δ: 1.25 (s, 6H, $2CH_3$), 2.61 (s, 2H, H-2), 2.85 (s, 2H, H-4), 3.97 (s, 3H, OCH_3), 4.06 (s, 3H, OCH_3), 7.08 (s, 1H, H-5), 7.59 (s, 1H, H-8), 8.08 (d, 1H, H-6′, J=9.5 Hz), 8.39 (dd, 1H, H-5′, J=9.5 and 2.5 Hz,), 9.18 (d, 1H, H-3′, J=2.5 Hz), 11.30 (s, 1H, N*H*). *Anal*. Calcd. for $C_{22}H_{22}O_7N_4$ (%): C, 58.15; H, 4.87; N, 12.32; Found (%): C, 57.92; H, 4.60; N, 12.50.

6,7-Dimethoxy-3,4-dihydro-2*H*-dibenzofuran-1-(2,4-dinitrophenylhydrazone) (5d). Compound **3b** (0.16 g, 0.6 mmol), 2,4-dinitrophenylhydrazine (0.13 g, 0.6 mmol) reacted in ethanol as described above to afford **5d**. Yield 0.14 g (51%), mp 250°C; ir (KBr) ν cm^{-1}: 3310 (NH), 1625 (C=N), 1580 (C=C), 1523-1344 (Ar-NO_2), 1300-1200 (Ar-O), 1075-1040 (CH_2-O); ^{1}H-NMR (400MHz/$CDCl_3$) δ: 2.29 (q, 2H, H-3, J=6.5 Hz), 2.83 (t, 2H, H-2, J=6.5 Hz), 3.00 (t, 2H, H-4, J=6.5 Hz), 3.97 (s, 3H, OCH_3), 4.05 (s, 3H, OCH_3), 7.09 (s, 1H, H-5), 7.60 (s, 1H, H-8), 8.08 (d, 1H, H-6′, J=9.5 Hz), 8.39 (dd, 1H, H-5′, J=9.5 and 2.5 Hz), 9.19 (d, 1H, H-3′, J=2.5 Hz), 11.46 (s, 1H, N*H*). *Anal*. Calcd. for $C_{22}H_{18}O_7N_4$ (%): C, 54.29; H, 4.07; N, 12.67; Found (%): C, 54.05; H, 3.92; N, 12.78.

6,7-(Ethylenedioxy)-3,3-dimethyl-3,4-dihydro-2*H*-dibenzofuran-1-(2,4-dinitrophenylhydrazone) (6a). Compound **4a** (0.40 g, 1.1 mmol), 2,4-dinitrophenylhydrazine (0.22 g, 1.1 mmol) reacted in ethanol as described above to afford **6a**. Yield 0.70 g (53%), mp 268°C; ir (KBr) ν cm^{-1}: 3310 (NH), 2978, 2850 (C-H), 1625 (C=N), 1573 (C=C), 1523-1344 (Ar-NO_2), 1300-1200 (Ar-O), 1075-1040 (CH_2-O); ^{1}H-NMR (400MHz/$CDCl_3$) δ: 1.28 (s, 6H, $2CH_3$), 2.55 (s, 2H, H-2), 2.79 (s, 2H, H-4), 4.53 (s, 4H, CH_2), 7.04 (s, 1H, H-5), 7.55 (s, 1H, H-8), 8.05 (d, 1H, H-6′, J=9.5 Hz), 8.40 (dd, 1H, H-5′, J=9.5 and 2.5 Hz), 9.13 (d,1H, H-3′, J=2.5 Hz), 11.45 (s, 1H, N*H*). *Anal*. Calcd. for $C_{22}H_{20}O_7N_4$ (%): C, 58.40; H, 4.42; N, 12.39; Found (%): C, 58.10; H, 4.58; N, 12.40.

6,7-(Ethylenedioxy)-3,4-dihydro-2*H*-dibenzofuran-1-(2,4-dinitrophenylhydrazone) (6b). Compound **4b** (0.10 g, 0.4 mmol), 2,4-dinitrophenylhydrazine (0.08 g, 0.4 mmol) reacted in ethanol as described above to afford **6b**. Yield 0.50 g (30%), mp 220°C; ir (KBr) ν cm^{-1}: 3310 (NH), 2978, 2850 (C-H), 1625 (C=N), 1580 (C=C), 1523-1345 (Ar-NO_2), 1300-1200 (Ar-O), 1075-1040 (CH_2-O); ^{1}H-NMR (400MHz/ $CDCl_3$) δ: 2.30 (q, 2H, H-3, J=6.5 Hz), 2.81 (t, 2H, H-2, J=6.5 Hz,), 2.97 (t, 2H, H-4, J=6.5 Hz), 4.10 (s, 4H, CH_2), 7.04 (s, 1H, H-5), 7.55 (s, 1H, H-8), 8.05 (d, 1H, H-6′, J=9.5 Hz), 8.40 (dd, 1H, H-5′, J=9.5 and 2.5 Hz), 9.13 (d, 1H, H-3′, J=2.5 Hz), 11.45 (s, 1H, N*H*). *Anal*. Calcd. for $C_{20}H_{16}O_7N_4$ (%): C, 56.60; H, 3.77; N, 13.21; Found (%): C, 56.51; H, 3.28; N, 13.30.

6,7-([1,4,7]-Trioxacyclononan)-3,3-dimethyl-3,4-dihydro-2*H*-dibenzofuran-1-(2,4-dinitrophenylhydrazone) (6c). Compound **4c** (0.065 g, 0.2 mmol), 2,4-dinitrophenylhydrazine (0.041 g, 0.2 mmol) reacted in ethanol as described above to afford **6c**. Yield 52 mg (52%), mp 232°C; ir (KBr) ν cm^{-1}: 3310 (NH), 2978, 2850 (C-H), 1625 (C=N), 1578 (C=C), 1523-1347 (Ar-NO_2), 1300-1200 (Ar-O), 1075-1040 (CH_2-O); ^{1}H-NMR (400MHz/ $CDCl_3$) δ: 1.78 (s, 6H, $2CH_3$), 2.59 (s, 2H, H-2), 2.83 (s, 2H, H-4), 4.01 (t, 4H, J=5 Hz, crown ether), 4.30 (t, 4H, J=5 Hz, crown ether), 7.06 (s, 1H, H-5), 7.59 (s, 1H, H-8), 8.06 (d, 1H, H-6′, J=9.5 Hz), 8.42 (dd, 1H, H-5′, J=9.5 and 2.5 Hz), 9.18 (d, 1H, H-3′, J=2.5 Hz), 11.43 (s, 1H, N*H*). *Anal*. Calcd. for $C_{24}H_{24}O_8N_4$ (%): C 58.06; H 4.83; N 11.29. Found (%): C 58.10; H 4.78; N 11.40.

6,7-([1,4,7,10]-Tetraoxacyclododecyl)-3,3-dimethyl-3,4-dihydro-2*H*-dibenzofuran-1-(2,4-dinitrophenylhydrazone) (6d). Compound **4d** (0.40 g, 1.1 mmol), 2,4-dinitrophenylhydrazine (0.22 g, 1.1 mmol) reacted in ethanol as described above to afford **6d**. Yield 0.25 g (41%), mp 248°C; ir (KBr) ν cm^{-1}: 3310 (NH), 2978, 2850 (C-H), 1625 (C=N), 1580 (C=C), 1523-1345 (Ar-NO_2), 1300-1200 (Ar-O), 1075-1040 (CH_2-O); ^{1}H-NMR (400MHz/$CDCl_3$) δ: 1.24 (s, 6H, $2CH_3$), 2.58 (s, 2H, H-2), 2.82 (s, 2H, H-4), 3.94 (t, 4H, J=4.5Hz, crown ether), 4.20 (t, 4H, J=4Hz, crown ether), 4.25 (t, 4H, J=4.5Hz, crown ether), 7.11 (s, 1H, H-5), 7.67 (s, 1H, H-8), 8.04 (d, 1H, H-6′, *J*=9.5 Hz), 8.41 (dd, 1H, H-5′, J=9.5 and 2.5 Hz,), 9.17 (d, 1H, H-3′, J=2.5 Hz), 11.45 (s, 1H, N*H*). ^{13}C-NMR ($CDCl_3$/TMS) δ: 30.99, 35.39, 39.27, 40.25, 71.99, 72.18, 73.27, 102.42, 113.09, 114.45, 118.05, 119.74, 125.59, 131.35, 132.13, 139.85, 146.77, 150.16, 151.59, 152.50, 152.96, 163.26. *Anal*. Calcd. for $C_{26}H_{28}O_9N_4$ (%): C 57.77; H 5.18; N 10.37; Found (%): C 57.90; H 5.04; N, 10.30.

6,7-([1,4,7,10]-Tetraoxacyclododecyl)-3,4-dihydro-2*H*-dibenzofuran-1-(2,4-dinitrophenylhydrazone) (6e). Compound **4e** (0.06 g, 0.17 mmol), 2,4-dinitrophenylhydrazine (0.034 g, 0.17 mmol) reacted in ethanol as described above to afford **6e**. Yield 47 mg (54%), mp 188°C; ir (KBr) ν cm^{-1}: 3310 (NH), 2978, 2850 (C-H), 1625 (C=N), 1575(C=C), 1523-1345 (Ar-NO_2), 1300-1200 (Ar-O), 1075-1040 (CH_2-O); ^{1}H-NMR (400MHz/$CDCl_3$) δ: 2.25 (q, 2H, H-3, J=6.5 Hz,), 2.81 (t, 2H, H-2, J=6.5 Hz), 2.92 (t, 2H, H-4, J=6.5 Hz), 3.82 (t, 4H, J=4Hz, crown ether), 4.16 (m, 8H, crown ether), 7.04 (s, 1H, H-5), 7.55 (s, 1H, H-8), 8.09 (d, 1H, H-6′, J=9.5 Hz), 8.44 (dd, 1H, H-5′, J=9.5 and 2.5 Hz), 9.18 (d, 1H, H-3′, J=2.5 Hz), 11.45 (s, 1H, N*H*). *Anal*. Calcd. for $C_{24}H_{24}O_9N_4$ (%): C 56.25; H 4.68; N 10.93. Found (%): C 56.18; H 4.50; N 11.05.

6,7-([1,4,7,10,13]-Pentaoxacyclododecyl)-3,3-dimethyl-3,4-dihydro-2*H*-dibenzofuran-1-(2,4-dinitrophenylhydrazone) (6f). Compound **4f** (0.69 g, 1.7 mmol), 2,4-dinitrophenylhydrazine (0.34 g, 1.7 mmol) reacted in ethanol as described above to afford **6f**. Yield 0.52 g (52% yield), mp 194°C; ir (KBr) ν cm^{-1}: 3310 (NH), 2978, 2850 (C-H), 1625 (C=N), 1580(C=C), 1523-1345 (Ar-NO_2), 1300-1200 (Ar-O), 1075-1040 (CH_2-O); ^{1}H-NMR (400MHz/$CDCl_3$) δ: 1.24 (s, 6H, $2CH_3$), 2.58 (s, 2H, H-2), 2.81 (s, 2H, H-4), 3.96 (t, 4H, J=4Hz, crown ether), 4.02 (t, 4H, J=4Hz, crown ether), 4.18 (t, 4H, J=4Hz, crown ether), 4.24 (t, 4H, J=4Hz, crown ether), 7.04 (s, 1H, H-5), 7.57 (s, 1H, H-8), 8.04 (d, 1H, H-6′, J=9.5 Hz), 8.39 (dd, 1H, H-5′, J=9.5 and 2.5 Hz), 9.16 (d, 1H, H-3′, J=2.5 Hz), 11.44 (s, 1H, N*H*); ^{13}C-NMR ($CDCl_3$/TMS) δ: 31.01, 36.01, 39.27, 40.25, 71.53, 71.58, 71.84, 72.38, 100.00, 109.31, 114.47, 117.96, 118.66, 125.63, 131.33, 132.07, 139.80, 146.79, 149.22, 152.32, 152.32, 152.72, 162.83; m/z 584. *Anal*. Calcd. for $C_{28}H_{32}O_{10}N_4$ (%): C 57.53; H 5.47; N 9.58; Found (%): C 57.46; H 5.38; N 9.70.

6,7-([1,4,7,10,13]-Pentaoxacyclododecyl)-3,4-dihydro-2*H*-dibenzofuran-1-(2,4-dinitrophenylhydrazone) (6g). Compound **4g** (0.15 g, 0.4 mmol), 2,4-dinitrophenylhydrazine (0.08 g, 0.4 mmol) reacted in ethanol as described above to afford **6g**. Yield 0.11 g (51%), mp 220°C; ir (KBr) ν cm^{-1}: 3310 (NH), 2978, 2850 (C-H), 1625 (C=N), 1575(C=C), 1523-1345 (Ar-NO_2), 1300-1200 (Ar-O), 1075-1040 (CH_2-O); ^{1}H-NMR (400MHz/ $CDCl_3$) δ: 2.23 (q, 2H, H-3, J=6 Hz), 2.40 (t, 2H, H-2, J=6 Hz), 2.52 (t, 2H, H-4, J=6 Hz), 3.78 (t, 4H, J=4.5 Hz, crown ether), 3.82 (t, 4H, J=4.5 Hz, crown ether), 4.06 (t, 4H, J=4.5 Hz, crown ether), 4.20 (t, 4H, J=4.5 Hz, crown ether), 7.03 (s, 1H, H-5), 7.50 (s, 1H, H-8), 8.04 (d, 1H, J=9.5 Hz, H-6′), 8.42 (dd, 1H, H-5′, J=9.5 and 2.5 Hz), 9.10 (d, 1H, H-3′, J=2.5 Hz), 11.45 (s, 1H, N*H*). *Anal*. Calcd. for $C_{26}H_{28}O_{10}N_4$ (%): C 56.11; H 5.03; N 10.10; Found (%): C 55.95; H 5.10; N 9.97.

6,7-([1,4,7,10,13,16]-Hexaoxacyclododecyl)-3,3-dimethyl-3,4-dihydro-2*H*-dibenzofuran-1-(2,4-dinitrophenylhydrazone) (6h). Compound **4h** (0.92 g, 2.1 mmol), 2,4-dinitrophenylhydrazine (0.41 g, 2.1 mmol) reacted in ethanol as described above to afford **6h**. Yield 0.65 g (50%), mp 216°C; ir (KBr) ν cm^{-1}: 3310 (NH), 2978, 2850 (C-H), 1625 (C=N), 1581 (C=C), 1523-1345 (Ar-NO_2), 1300-1200 (Ar-O), 1075-1040 (CH_2-O); ^{1}H-NMR (400MHz/$CDCl_3$) δ: 1.78 (s, 6H, $2CH_3$), 2.59 (s, 2H,

H-2), 2.83 (s, 2H, H-4), 3.67-4.31 (m, 20H, crown ether), 7.06 (s, 1H, H-5), 7.59 (s, 1H, H-8), 8.06 (d,1H, H-6′, J=9.5 Hz), 8.42 (dd, 1H, H-5′, J=9.5 and 2 Hz), 9.17 (d, 1H, H-3′, J=2 Hz), 11.45 (s, 1H, N*H*). *Anal*. Calcd. for $C_{30}H_{36}O_{11}N_4$ (%): C 56.90; H 5.70; N 9.00; Found (%): C 56.80; H 5.68; N 9.15.

6,7-([1,4,7,10,13,16]-Pentaoxacyclododecyl)-3,4-dihydro-*2H*-dibenzofuran-1-(2,4-dinitrophenylhydrazone) (**6i**). Compound **4i** (0.05 g, 0.1 mmol), 2,4-dinitrophenylhydrazine (0.023 g, 0.1 mmol) reacted in ethanol as described above to afford **6i**. Yield 31.5 mg (41%), mp 218°C; ir (KBr) ν cm^{-1}: 3310 (NH), 2978, 2850 (C-H), 1625 (C=N), 1578 (C=C), 1523-1345 (Ar-NO_2), 1300-1200 (Ar-O), 1075-1040 (CH_2-O); ^{1}H-NMR (400MHz/ $CDCl_3$) δ: 2.30 (q, 2H, H-3, J=6Hz), 2.56 (t,2H, H-2, J=6 Hz), 3.00 (t, 2H, H-4, J=6 Hz), 3.80 (t, 4H, J=6 Hz, crown ether), 4.00 (t, 4H, J=5 Hz, crown ether), 4.05 (t, 4H, J=5 Hz, crown ether), 4.20 (t, 4H, J=5 Hz, crown ether), 4.30 (t, 4H, J=5 Hz, crown ether), 7.03 (s, 1H, H-5), 7.50 (s, 1H, H-8), 8.04 (d, 1H, H-6′, J=8.5 Hz), 8.42 (dd, 1H, H-5′, J=9 and 2 Hz), 9.10 (d, 1H, H-3′, J=2Hz), 11.45 (s, 1H, N*H*). *Anal*. Calcd. for $C_{28}H_{32}O_{11}N_4$ (%): C 56.00; H 5.33; N 9.33; Found (%): C 55.70; H 5.20; N 9.45.

Acknowledgements. This work was supported by The Scientific and Technological Research Council of Turkey (TUBİTAK) with TBAG-AY/397(104T384) project.

REFERENCES

[1] C. J. Pederson, *Angew. Chem. Int. Ed. Engı.,* **27**, 1021 (1988).

[2] P C. J. Pederson and H. K. Frenssdorff, *Angew. Chem.,* **84**, 16 (1972).

[3] J. J. Christensen, D. J. Eathough and R. M. Izatt, *Chem. Rev*., **74**, 351 (1974).

[4] J. M. Lehn and J. P. Sauvage, *J. Am. Chem. Soc*., **97**, 6700 (1975).

[5] G. W. Gokel and H. D. Durts, *Synthesis,* 168 (1976).

[6] M. Takagi, H. Nakamura and K. Ueno, *Anal. Lett.,* **10**, 1115 (1977).

[7] M. Bulut, B. Yılmaz, M. Yapıcı and M. V. Kahraman, *J. Inclusion Phenom.,* **26**, 39 (1996).

[8] S. Abdurrahmanoğlu, C. Gündüz, Ü. Çakır, B. Çiçek and M. Bulut, *Dyes and Pigments,* **65**, 197 (2005).

[9] C. Gündüz, Ü. Salan, N. Özkul, İ. Başaran, Ü. Çakır and M. Bulut, *Dyes and Pigments,* **71**, 161 (2006)

[10] Ü. Salan and M. Bulut, *Heterocycles,* **68**, 237 (2006).

[11] H. W. Wanzlick, R. Gritzky and H. Heidenpriem, *Chem. Ber.,* **5**, 96 (1963).

[12] Z. Grujic, I. Tabakovic and M. Trkovnik, *Tetrahedron Lett*., 4823 (1976).