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# Novel oxadiazole- and triazole-based calixarene derivatives: synthesis and extraction properties

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## Abstract

*Two new calixarene derivative compounds bearing oxadiazole and triazole groups were synthesized. The final products were illuminated by using $^{1}H$-NMR, $^{13}C$-NMR, FT-IR and HR-MS. The extraction efficiency of these compounds was investigated in the removal of methyl orange. In addition, the effect of $H^{+}$ ion concentration in extraction studies conducted in different pH ranges and the effect of NaCl concentration on the percentage of extraction was examined. The results obtained showed that the percentage of extraction was highly dependent on the $H^{+}$ ion concentration. It was found that the percentage of methyl orange removal was 53.3% for triazole derivatives 5.*

***Keywords:*** *Calixarene, oxadiazole, triazole, extraction.*

# Yeni okzadiazol ve triazol bazlı kaliksaren türevlerinin sentezi ve ekstraksiyon özellikleri

## Öz

*Bu çalışmada, okzadiazol ve triazol türevi taşıyan iki yeni kaliksaren türevi bileşik sentezlendi. Elde edilen nihai ürünlerin yapıları $^{1}H$-NMR, $^{13}C$-NMR, FT-IR ve HR-MS analizleri ile aydınlatıldı. Bu bileşikler ile sıvı-sıvı ekstraksiyonu yapılarak sulu çözeltideki metil oranjın uzaklaştırılmasında etkinlikleri değerlendirildi. Ayrıca ekstraksiyon yüzdesi üzerine $H^{+}$ iyonu konsantrasyonu ve NaCl konsantrasyonunun etkisi incelendi. Elde edilen sonuçlar ekstraksiyon yüzdesinin $H^{+}$ iyonu*

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*konsantrasyonuna bağlı olduğunu gösterdi. Triazol türevi 5 için sulu ortamdan metil oranjın uzaklaştırılma yüzdesi % 53.3 olarak bulundu.*

***Anahtar kelimeler:*** *Kaliksaren, okzadiazol, triazol, ekstraksiyon.*

## 1. Introduction

The phenolic hydroxyl groups and the para positions of calixarenes can easily be functionalized to obtain molecules with desired sizes [1-5]. In addition, the meta positions and the methylene bridges can also be functionalized [6-9]. Obtaining different conformations by using different reagents is another aspect that makes this study an attractive one [10-12]. Since calixarene skeleton is very versatile and can be converted to many compounds, it has an important role in host-guest chemistry [13-15]. For this reason, many extraction and fluorescence studies have been performed with these compounds [16-20]. Especially, in extraction studies, calixarene derivatives seem to be particularly effective in removing carcinogenic azo dyes [21-23]. Since the derivatives of these compounds and their polymeric structures show good results in the removal of azo dyes, this makes the synthesis of calixarene derivatives important in such studies [24-27].

1,3,4-oxadiazole and 1,2,4-triazole derivatives are known to exhibit biological activities such as anticancer, antimicrobial, antifungal and antiviral [28-32]. In addition to biological properties, 1,3,4-oxadiazole has a great advantage in material science due to its various electronic properties [33-35]. These two structures can act as ligands and easily interact with some metal ions because of their heteroatoms [36, 37]. In the literature, calixarene derivatives with heterocyclic structure show very effective results in removing azo dyes [21-23,24]. Although different methods and structures are used, the calixarene molecule appears to be a good host for azo dyes.

Since azo dyes are not biodegradable, they emerge as an important environmental problem in waste water [38]. In addition to environmental problems, azo dyes show various toxic properties in the human body such as cancer [39, 40]. One of the anionic dyes used academically and industrially among azo dyes is methyl orange [39, 41]. Therefore, studies on removing azo dyes such as methyl orange from wastewater have increased considerably. The structure of methyl orange is shown in figure 1.

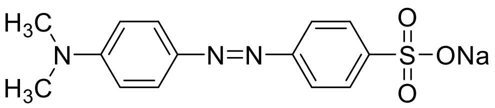


Figure 1. Structure of methyl orange

In our study, we present two novel calixarene derivatives containing 1,2,4-triazole and 1,3,4-oxadiazole. The extraction efficiency of these two compounds were investigated in the removal of methyl orange. In addition, the effect of $H^+$ ion concentration in extraction studies conducted in different pH ranges and the effect of NaCl concentration on the percentage of extraction was examined.

## 2. Material and method

### 2.1. General

All chemical reagents and solvents were purchased from Merck, Acros and Sigma-Aldrich and used without any purification. Solvents were dried with 3 Å molecular sieve activated and used analytical grade. Varian Mercury Plus 300 MHz was used for $^{1}H$ and $^{13}C$ NMR analysis. Fourier Transform Infrared analyses were performed on the PerkinElmer Frontier FT-IR Spectroscopy. Waters SYNAPT G1 MS was used for HRMS results. Shimadzu model UV-1700 spectrophotometer was used for UV-Vis. measurements. Thin Layer chromatography (TLC) purchased from Merck was used to monitorize all reactions. Silica gel 60 purchased from Merck was used for column chromatography.

### 2.2. Synthesis of 25,27-Bis(4-bromobutoxy)-26,28-dihydroxy-5,11,17,23-tetra(tert-butyl)calix[4]arene

Compound 2 (1 g, 1.54 mmol), 1,4-Dibromobutane (3.33 g, 15.4 mmol) and potassium carbonate (223.6 mg, 1,62 mmol) were taken in a flask and added 80 ml $CH_3CN$. The mixture was refluxed for 24h. Organic solvent was evaporated under vacuum. The residue was dissolved 50 ml $CH_2Cl_2$ and 50 ml water. The organic phase was washed twice more with water. The organic phase was dried over $MgSO_4$. The solvent was evaporated under vacuum. The residue was purified by using column chromatography on silica gel with $CH_2Cl_2$:n-Hexane (2:3). Yield: 66.7%

### 2.3. Synthesis of 25,27-Bis[4-(5-(pyridin-3-yl)-1,3,4-oxadiazol-2-ylthio)butoxy]-26,28-dihydroxy-5,11,17,23-tetra(tert-butyl)calix[4]arene

5-(3-Pyridyl)-1,3,4-oxadiazole-2-thiol (42.2 mg, 0.24 mmol) and potassium carbonate (31.5 mg, 0.23 mmol) were taken in a flask and added 30 mL $CH_3CN$. The mixture was refluxed for 30 minutes. Compound 3 (0.1 g, 0.11 mmol) in 20 mL $CH_3CN$ was added to the mixture drop by drop. The reaction mixture was refluxed for an additional 24 h. Organic solvent was evaporated under vacuum. The residue was dissolved 50 mL $CH_2Cl_2$ and 50 mL water. The organic phase was washed twice more with water. The organic phase was dried over $Na_2SO_4$. The solvent was evaporated under vacuum. The residue was purified by using column chromatography on silica gel with $CH_2Cl_2$:$CH_3OH$ (40:1). Yield: 63.5%

$^{1}H$ NMR (CHLOROFORM-d, 300MHz): δ (ppm) 9.21 (br. s, 2H), 8.74 (br. s, 2H), 8.24 (d, *J*=7.9 Hz, 2H), 7.41 (s, 4H), 7.04 (s, 4H), 6.80 (s, 4H), 4.24 (d, *J*=12.9 Hz, 4H), 4.06 (t, *J*=5.9 Hz, 4H), 3.60 (t, *J*=7.0 Hz, 4H), 3.31 (d, *J*=13.2 Hz, 4H), 2.29 - 2.42 (m, 4H), 2.17 - 2.29 (m, 4H), 1.29 (s, 18H), 0.96 (s, 18H); $^{13}C$ NMR (CHLOROFORM-d, 75MHz): δ (ppm) 165.5, 163.8, 152.4, 150.8, 149.9, 147.8, 147.2, 141.8, 134.0, 132.7, 127.9, 125.8, 125.3, 123.9, 120.4, 76.0, 34.2, 34.0, 32.9, 31.9, 31.2, 29.2, 26.5; FTIR ($cm^{-1}$): 3394.9, 1602.9; HRMS (ESI-MS) m/z: $[M+H]^+$ Calcd for $C_{66}H_{79}N_6O_6S_2$ 1115.5503; found 1115.5466.

### 2.4. Synthesis of 25,27-Bis[4-(5-(pyridin-3-yl)-4H-1,2,4-triazol-3-ylthio)butoxy]-26,28-dihydroxy-5,11,17,23-tetra(tert-butyl)calix[4]arene

5-(3-pyridyl)-4H-1,2,4-triazole-3-thiol (0.21 g, 1.2 mmol) and potassium carbonate (165 mg, 1.2 mmol) were taken in a flask and added 60 mL THF. The mixture was stirred for 2 hours at room temperature. Compound 3 (0.5 g, 0.54 mmol) was added to the mixture. The reaction mixture was stirred for an additional 24 h. The temperature was adjusted to 50 °C and stirred for 2 days. Organic solvent was evaporated under vacuum.

The residue was dissolved 70 mL $CH_2Cl_2$ and 70 mL water. The organic phase was washed twice more with water. The organic phase was dried over $Na_2SO_4$. The solvent was evaporated under vacuum. The residue was purified by using column chromatography on silica gel with $CH_2Cl_2$:$CH_3OH$ (40:1 to 20:1). Yield: 71.5%
$^1$H NMR (CHLOROFORM-d, 300MHz): δ (ppm) 9.35 (br. s., 2H), 8.64 (d, *J*=4.7 Hz, 2H), 8.35 (d, *J*=6.4 Hz, 2H), 7.49 (br. s., 2H), 7.32 - 7.42 (m, 2H), 7.06 (s, 4H), 6.80 (s, 4H), 4.28 (d, *J*=12.9 Hz, 4H), 4.01 (br. s., 4H), 3.41 (br. s., 4H), 3.33 (d, *J*=12.9 Hz, 4H), 2.14 (br. s., 8H), 1.29 (s, 18H), 0.97 (s, 18H); $^{13}$C NMR (CHLOROFORM-d, 75MHz): δ (ppm) 159.0, 155.6, 150.6, 150.0, 149.9, 147.5, 147.3, 142.1, 134.5, 132.8, 128.1, 126.7, 125.8, 125.4, 124.1, 76.2, 34.2, 34.1, 33.5, 32.0, 31.3, 29.3, 26.9. FTIR ($cm^{-1}$): 3362.7, 1604.8; HRMS (ESI-MS) m/z: $[M+H]^+$ Calcd for $C_{66}H_{81}N_8O_4S_2$ 1113.5822; found 1113.5769.

### 2.5. Extraction studies

Extractions were performed following similar methods in the literature [21-23]. Firstly, $1x10^{-5}$ M solutions of methyl orange containing 0.2 mol/L NaCl at pH = 3, 5, 7 and 9 and $1x10^{-3}$ M solutions of compounds 4 and 5 in dichloromethane were prepared. 10 mL of dye solution and 10 mL of calixarene solution were mixed at 25 °C and 150 rpm for 1 hour. The phases were allowed to separate for 30 minutes. The water phase was taken and its absorbance was measured in UV-Vis spectrophotometry at 463 nm. The percentage of extraction was calculated using the equation below [21-23].

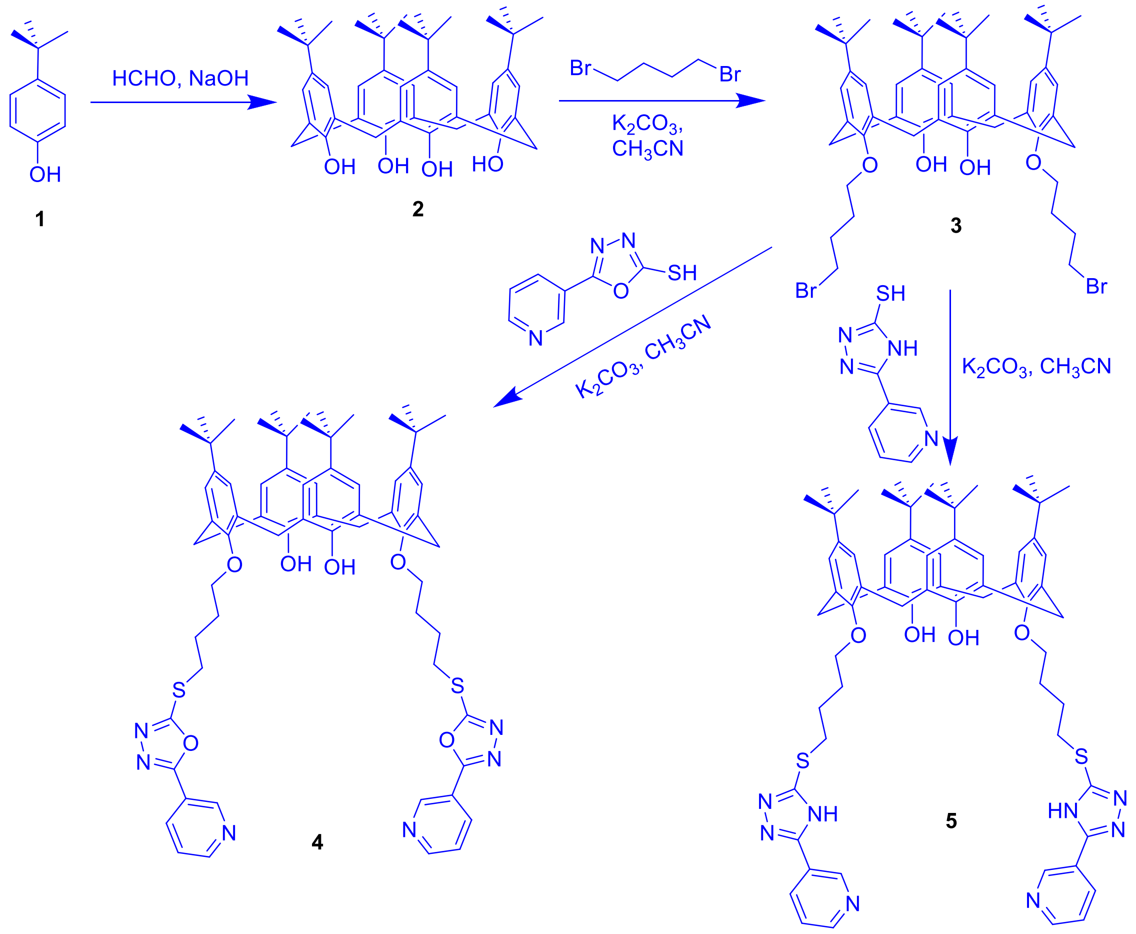
$$\%\, Extraction = \frac{C_1 - C_2}{C_1} \times 100$$

The methyl orange concentration in the initial solution is $C_1$. The methyl orange concentration in the final solution is $C_2$.

## 3. Result and discussion

In order to obtain these structures, first, *p-tert*-butylcalix[4]arene was synthesized by using the procedure from Gutsche [42]. In the next step, two equivalent 1,4-dibromobutane was attached to the two phenolic hydroxyl groups [43]. Finally, dibromo calixarene derivative was treated with 5-(3-pyridyl)-4H-1,2,4-triazole-3-thiol and 5-(3-pyridyl)-1,3,4-oxadiazole-2-thiol in $K_2CO_3$/$CH_3CN$ system. The synthetic steps are shown in scheme 1 below. The final products were characterized by using $^1$H NMR, $^{13}$C NMR, FT-IR and HRMS. The compounds 4 and 5 which produced in three steps were afforded in 63.5% and 33% yield, respectively. The $^1$H NMR spectral data of Compound 4 showed that the methylene protons attached to the bromide atom shifted from 3.65 ppm to 3.60 ppm. The presence of pyridine protons at 8.24, 8.74 and 9.21 ppm in the aromatic region as well as phenol protons support the structure. For the compound 4, the presence of fifteen carbons of the oxadiazole, pyridine and calixarene were confirmed by $^{13}$C NMR. In addition, the methylene carbon attached to sulfur atom were found under $CDCl_3$ peaks around 77 ppm in $^{13}$C NMR spectra. HRMS spectrometry gave 1115.5466 $[M+H]^+$ which supports the accuracy of the structure. In compound 5, the methylene protons attached to sulphur atom shifted from 3.65 ppm to 3.41 ppm. In addition, the $^1$H-NMR spectra of the two products obtained showed that the presence of two doublet peaks of methylene protons around 3.32 and 4.26 ppm with characteristic geminal coupling constants confirms that cone conformation is preserved.

In the aromatic region, three peaks indicating the presence of the pyridine were observed at 8.35, 8.64 and 9.35 ppm. 15 peaks due to calixarene, triazole and pyridine were observed in aromatic region in $^{13}$C NMR. The methylene carbons attached to sulphur atom were seen under the $CDCl_3$ peaks around 77. Mass spectrometry gave 1113.5769 $[M+H]^+$ which confirms the formation of the structure.



Scheme 1. The synthetic route to the compounds 4 and 5

After the synthesis of the desired molecules, extraction studies were performed. In previous studies, it is seen that NaCl contributes significantly to the extraction efficiency [39]. Therefore, the initial dye solutions containing 0.2 mol/L NaCl were prepared at different pH ranges. pH ranges of 3, 5, 7 and 9 were selected in the study. Due to phenolic protons on calixarene, pH = 11 was not studied. In the extraction with compound 4, a very small amount of methyl orange was found to be extracted at pH = 3 and pH = 9. While the extraction efficiency was 14.1% at pH = 3, it was 14.7% at pH = 9. At the other two pH levels, it was observed that methyl orange could not be removed at all. In the extraction with compound 5, it was determined that the extraction increased significantly at pH = 3 and was found to be 53.3%. At pH = 5, 7 and 9, it was measured as 4.2%, 0% and 18.6%, respectively. The extraction percentages for compound 4 and compound 5 are shown in figure 2. Since the pyridine groups on these two compounds could not show their basic character at pH=7, the extraction percentages were found to be zero for both compounds. At pH = 5, however, the fact that compound 5 has a slight difference on the extraction percentage is due to the weak basic character of the triazole group on the structure. These data support that the basic groups are protonated in the acidic solution and methyl orange is transported by hydrogen bonding.

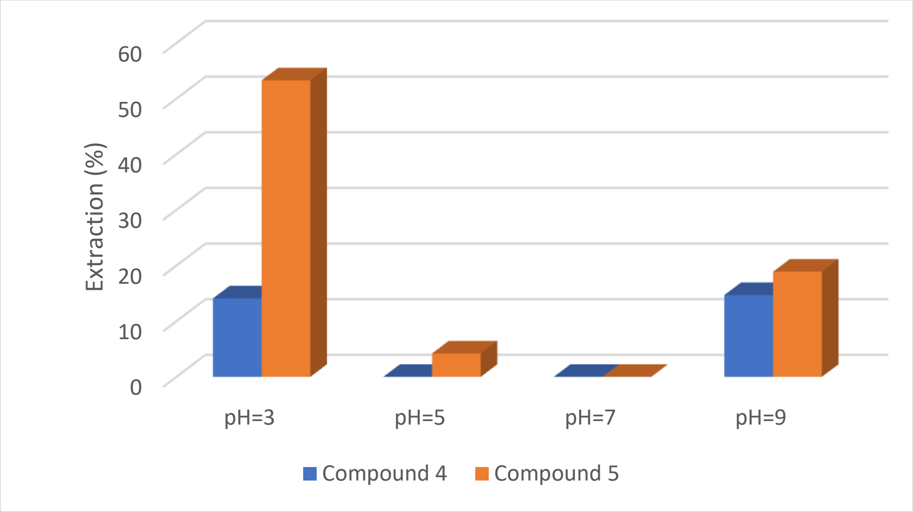


Figure 2. Percentage extraction values at different pH for compound 4 and compound 5

Sodium chloride has a significant effect in the removal of these structures because it provides ionic balance and significantly reduces the solubility of azo dyes [22, 23]. Therefore, methyl orange solutions containing different concentrations of NaCl were prepared to examine the effect on extraction efficiency. This study was conducted at the pH at which both molecules are most effective. pH = 9 was selected for compound 4, while pH = 3 was selected for compound 5. As expected for compound 4, the increase in NaCl concentration slightly increased the extraction percentage, while for compound 5 it was observed to decrease. The effect of NaCl concentration on the extraction percentage is shown in figure 3. For compound 4, the solubility of methyl orange decreased with the common ion effect, while for compound 5, a decrease in the extraction percentage was observed due to the commutative ion interferences [22, 23].

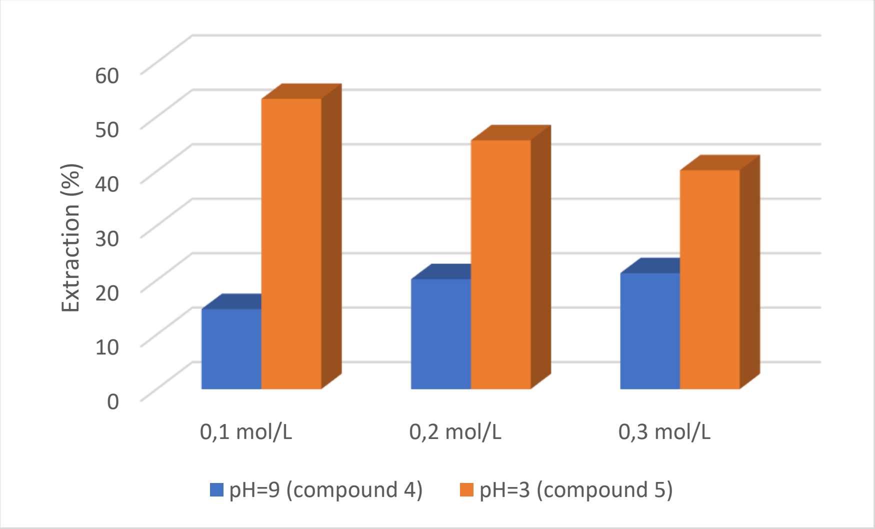


Figure 3. Effect of NaCl on percentage of extraction at pH = 9 for compound 4 and at pH = 3 for compound 5

Although there is only one different atom between compound 4 and compound 5, this difference in extraction percentage can be explained by the weak basic character of triazole. It is thought that the triazole ring is protonated under acidic conditions and as a result, it is transported by hydrogen bonding with the sulfonate oxygen on methyl orange. The proposed structure for the transport of methyl orange is shown in figure 4.

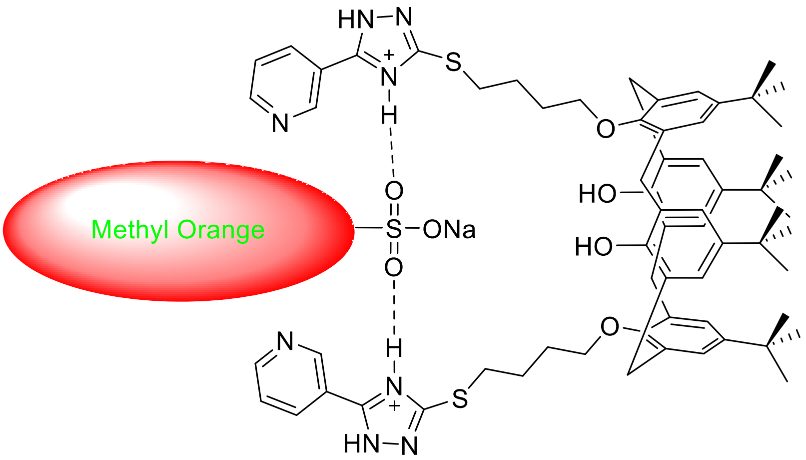


Figure 4. The proposed structure for the transport of methyl orange at pH=3

## 4. Conclusion

In this study, two novel calixarene derivatives containing oxadiazole and triazole groups were described. The structures of these compounds were characterized by spectroscopic techniques such as $^{1}$H-NMR, $^{13}$C-NMR, FT-IR and HR-MS. Liquid-liquid extraction of methyl orange, known as azo dye, was carried out at different pH values. The results showed that the highest percentage of extraction was 53.3% with compound **5** at pH=3. In addition, the extraction efficiency was found to be based on ionic strength and pH.

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