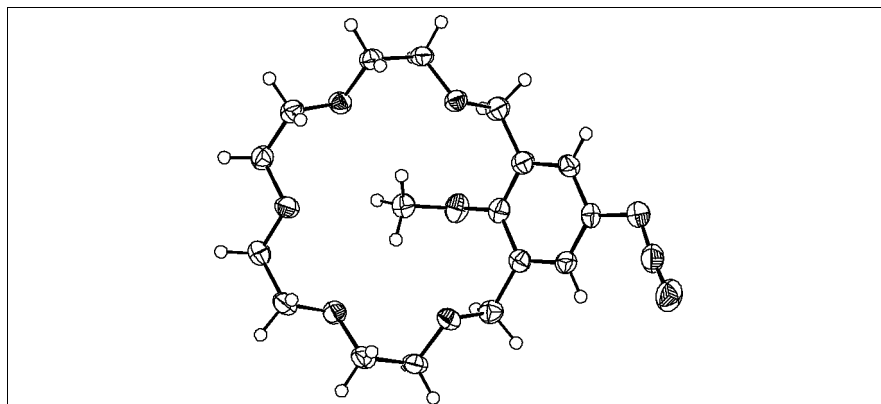


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5-Azido-2-methoxy-1,3-xylyl-18-crown-5 has been prepared by reacting *p*-toluenesulfonyl azide with the carbanion generated from the reaction of 5-bromo-2-methoxy-1,3-xylyl-18-crown-5 with *n*-butyl lithium. The asymmetric  $N_3$  stretch of this product has been observed as a single band at  $2110\text{ cm}^{-1}$  in dichloromethane solution. Addition of solid NaSCN, KSCN and CsSCN shifts this band to  $2115$ ,  $2113$  and  $2112\text{ cm}^{-1}$ , respectively. Computational studies of this azide at the B3LYP-6-31G\* level in the presence and absence of  $\text{Na}^+$  predicted these bands to be at  $2173\text{ cm}^{-1}$  and  $2184\text{ cm}^{-1}$ . For the salt-containing solutions, additional bands were observed at  $2066\text{ cm}^{-1}$ ,  $2056\text{ cm}^{-1}$  and  $2055\text{ cm}^{-1}$ , respectively, which are in the range expected for CN stretches. The X-ray structure of this azide has been determined. The terminal and internal N-N bond lengths were found to be  $1.127(2)$  and  $1.245(2)\text{ \AA}$ , respectively, which is the usual pattern for aromatic azides. The crown ether is looped over the face of the aromatic ring resulting in an angle of  $38.94^\circ$  between the plane defined by the aromatic ring and that defined by the five ring oxygen atoms. In addition, the  $\text{CH}_3$  group is rotated out of the plane of the phenyl ring with C1-C18-O181-C182 and C17-C18-O181-C182 dihedral angles of  $93.81(14)^\circ$  and  $-90.54(14)^\circ$ , respectively.

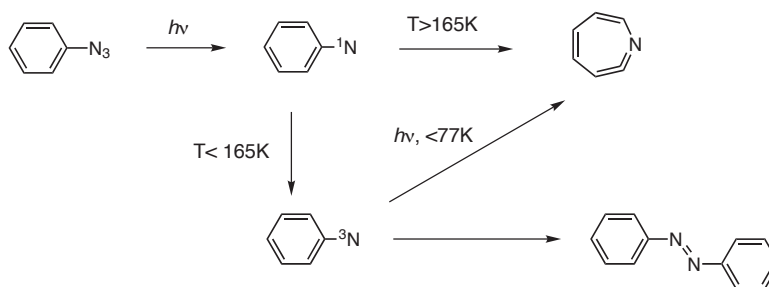
*J. Heterocyclic Chem.*, **43**, 689 (2006).

### Introduction.

The physical chemistry of aryl azides, which has been recently reviewed, [1, 2] continues to be studied extensively for several reasons including their interesting and complex photochemistry and their potential for useful applications. In regard to the latter, they can be used as

photoaffinity labels for biomolecules, [3, 4] photoresist linking agents, [5] and in the preparation of light activated polymer surfaces [6,7]. In regard to the former, the course of photochemical decomposition of phenyl azides has been established by laser flash photolysis (LFP) methods [8-12] and both time-resolved infrared [13] and Raman [14]

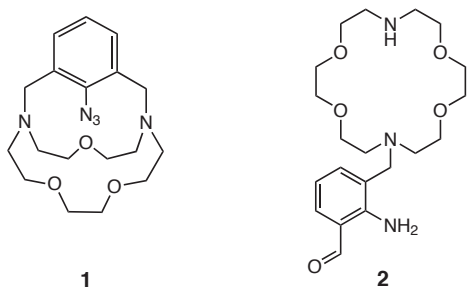
Scheme 1



Simplified Description of Photochemical Decomposition of Phenyl Azide

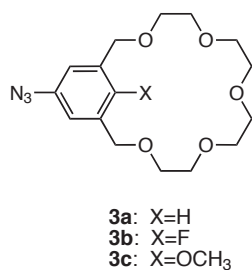
spectroscopy to proceed *via* the singlet nitrene, which may undergo either a rapid ring expansion reaction to form didehydroazepine or intersystem crossing (ISC) to form the triplet which subsequently dimerizes [8-12]. At ambient temperatures, singlet phenyl nitrenes have lifetimes of about 1 ns. In general, ring expansion is favored at higher temperatures, and ISC is favored at lower temperatures.

Recently, Bucher and coworkers reported a series of cryptand-like molecules functionalized with intraannular azido groups of the type shown in **1** [15-17]. LFP studies of **1** indicate that the singlet nitrene is formed initially [17]. This nitrene is reasonably long-lived as a result of the substitution in both *ortho*-positions, which is known to slow the rate of rearrangement to didehydroazepine species [11]. Thus at room temperature ISC may compete with rearrangement, and both the iminyl radical (from triplet hydrogen abstraction) and ketenimine were



observed. Several photolysis products of **1** were observed including **2**, which presumably arises from the iminyl intermediate. Further, it was determined that the presence of Na<sup>+</sup> or K<sup>+</sup> ions had minimal effect on these experimental outcomes.

In view of these interesting results and our continuing interest in functionalized crown ethers, we began exploring the



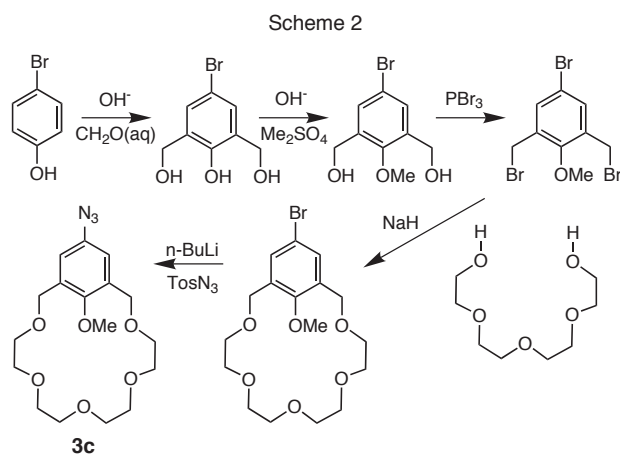
possibilities of incorporating azides into crown ether groups where the azido groups were electronically coupled to, but remotely located from, crown ether groups. Since we were unable to locate any other reported examples of such hybrid molecules, we elected to attempt the synthesis of molecules of the type shown in **3** not only in anticipation of comparing the photochemical properties of these with **1** but also of using 3 + 2 cycloaddition reactions to prepare, for example, novel *bis*

crowns. The 1,3-xylyl-18-crown-5 system was selected because the synthetic methods for a variety of these systems are well developed, and they are usually crystalline [18-20]. For the specific initial target, the system with the methoxy group (**3c**) was selected for three reasons. First, this oxygen provides an electronic link to the azide group which could be helpful in future photochemical studies. In addition, this group is an immediate precursor for both the phenol and phenoxide derivatives [18], and **3c** is also the most readily obtained crown ether of the group shown in **3**. Herein we report the synthesis, properties and X-ray structure of the target azide **3c**.

## Results and Discussion.

### Synthesis.

The title compound was prepared in modest yield by reacting the carbanion generated by Li-Br exchange with tosyl azide at low temperature (see Scheme 2) [21]. The product was readily purified by flash chromatography with the purest product appearing in the first fractions. We have not attempted to optimize the yields of the azide because the synthesis, though not trivial, involves inexpensive starting materials, tetraethylene glycol and 4-bromo-2,6-bis(bromomethyl)anisole, and the crown forming reaction can readily provide 60-70 % yield of the immediate precursor [20]. Compound **3c** is reactive, but can be maintained if stored in a freezer. The spectroscopic properties of the molecule are unremarkable, but entirely consistent with the functional groups present. As expected, the chemical shifts observed for the aliphatic protons are nearly identical to those observed for the immediate precursor. The aromatic signals are somewhat different in that they appear at 7.4 and 6.9 ppm for the bromo- and azido- compounds, respectively. This is the type of shift expected in view of the multiplets observed for bromobenzene and phenyl azide range from 7.25-7.60 and 7.04 to 7.39 ppm for the former and latter, respectively.



Synthesis of Crown Ether System, **3c**

We first attempted to prepare the azide using an approach that involved nitrating the 4- position of 2-methoxy-1,3-xylyl-18-crown-5 as described previously for 2-hydroxy-1,3-xylyl-18-crown-5 [18]. In our hands the procedure, which involved using sodium nitrite and nitric acid, did not provide acceptable yields. This could be due to the orientation of the OCH<sub>3</sub> group which is, as reported for related molecules and will be further discussed, forced to be out of the plane of the phenyl ring by the neighboring benzylic groups. In the absence of steric hindrance, the planar arrangement has been clearly established by X-ray [22, 23], optical spectroscopic [24], TOFMS [25] and computational [26] methods, and this arrangement is necessary for the OCH<sub>3</sub> to have its full activating effect. Such is not the case for the OH group which is not only a better donor than an OCH<sub>3</sub> group [27] but also made potentially more activating by the presence of a ring oxygen-to-hydrogen hydrogen bond [18].

#### Infrared Studies.

The asymmetric N<sub>3</sub> stretch of this azide with substituents in the 1 and 3 positions was of interest for several reasons. First, for most *meta* and *para* substituted aryl azides this vibration is observed as two bands rather than the expected single band [28-31]. This is the result of Fermi resonance where the mixing of a fundamental band with an overtone or combination band with the same symmetry gives rise to two bands [32, 33]. In contrast however, it is a single band for both the *meta* and *para* methoxy-substituted phenyl azides and **1**. In view of this situation along with the possibilities of shifting the position of the asymmetric band upon addition of alkali metal ions prompted our investigation of the infrared spectrum of **3c**. In the absence of ions, the asymmetric stretch is readily apparent as an intense singlet at 2110.1 ± 0.1 cm<sup>-1</sup> when recorded in CH<sub>2</sub>Cl<sub>2</sub> solution. When solid NaSCN, KSCN or CsSCN is added to the dichloromethane solution, this absorption appears at 2115 cm<sup>-1</sup>, 2113 cm<sup>-1</sup> or 2112 cm<sup>-1</sup>, respectively. This shift of the azide band to higher energy is consistent with the conclusion that it arises from the decreased electron density caused by crown complexation of sodium ions.

Reported data that show the same trend arose from studies of the *meta*- and *para*-substituted methoxy phenyl azides which have provided single bands at 2116 and 2111 cm<sup>-1</sup>, respectively [31]. The Hammett parameters for OCH<sub>3</sub> groups in these positions are 0.12 and -0.27, respectively clearly indicating the lower degree of electron density donation in the *meta* isomer [27]. During our studies, the sharp band from dichloromethane at 2035.8 ± 0.1 cm<sup>-1</sup> was used as the standard. Additionally, the spectrum of phenyl azide was also recorded in dichloromethane and the two bands were observed at

Table 1  
Selected Crystallographic Data for C<sub>17</sub>H<sub>25</sub>N<sub>3</sub>O<sub>6</sub>.

formula	C <sub>17</sub> H <sub>25</sub> N <sub>3</sub> O <sub>6</sub>
fw, g/mol	367.41
space group	P2 <sub>1</sub> /n (No. 14)
cell dimens at 150 K	
a, Å	11.5185(8)
b, Å	8.7423(4)
c, Å	18.7687(13)
β, deg	98.031(4)
V, Å <sup>3</sup>	1871.5(2)
Z, molecules/cell	4
d <sub>calc</sub> , g cm <sup>-3</sup>	1.30
2 θ range, deg	4.38-55.73
Total reflections	14,210
unique data	4437
data used in refinement	4427
R <sub>int</sub> 0.052	
data with I > 2.0σ(I)	2416
largest shift/esd in final cycle	0.00
R(F <sub>o</sub> )	0.049
R <sub>w</sub> (F <sub>o</sub> <sup>2</sup> )	0.104

Table 2  
Selected Bond Angles (deg) for **3c**

C16-O15-C14	112.19(13)	smallest
C2-O3-C4	113.21(14)	largest
O12-C13-C14	107.21(14)	smallest
O9-C8-C7	109.73(15)	largest
C18-O181-C182	116.28(17)	
N203-N202-N201	173.4(2)	
N202-N201-C20	116.28(17)	

Table 3  
Selected Bond Distances (Å) for **3c**

N-202-N203	1.127(2)	
N201-N202	1.245(2)	
N201-C20	1.427(2)	
C18-O181	1.379(2)	
O15-C14	1.426(19)	longest
O12-C11	1.412(2)	shortest
C16-C17	1.504(2)	longest
C4-C5	1.494(3)	shortest
C1-C18	1.399(3)	longest
C17-C21	1.384(3)	shortest

Table 4  
Selected Torsion Angles (deg) for **3c**

C2-C1-C18-C17	173.7(2)	C18-C1-C2-O3	-80.9(2)
C4-O3-C2-C1	175.1(1)	C2-O3-C4-C5	-162.0(1)
O3-C4-C5-O6	67.5(2)	C7-O6-C5-C4	-180.0(2)
C5-O6-C7-C8	175.7(2)	O6-C7-C8-O9	-74.5(2)
C10-O9-C8-C7	-175.5(2)	C8-O9-C10-C11	177.0(2)
O9-C10-C11-C12	76.9(2)	C13-O12-C11-C10	179.8(1)
C11-O12-C13-C14	177.3(1)	O12-C13-C14-O15	-71.9(2)
C16-O15-C14-C13	164.6(2)	C14-O15-C16-C17	-168.5(2)
O15-C16-C17-C18	81.1(2)	C16-C17-C18-C1	-174.0(2)

2129 and 2098 cm<sup>-1</sup> whereas published values are 2134 and 2102 cm<sup>-1</sup> [31], and the position of these bands did not change upon the addition of NaSCN. It has

previously been concluded that the asymmetric stretch of phenyl azides is not very sensitive to the nature of the substituent in the *para* position [30, 31]. However, most spectra are complicated by Fermi resonance, which provide perturbed data from which the unperturbed frequencies, can only be calculated if the overtone or combination band frequency can be identified. In view of this situation, data from systems like the anisole derivatives or **3c** may provide the best insights into any trends in substituent effects.

To provide additional information about the infrared spectra, computational studies of **3c** were performed at the B3LYP-6-31G\* level of theory [34-36]. These predicted the asymmetric stretches for the free and sodium ion complexed crowns to be at 2173  $\text{cm}^{-1}$  and 2184  $\text{cm}^{-1}$ , gas phase corrected respectively. The normal modes corresponding to these frequencies indicate that these stretches are largely uncoupled from the rest of the system. The change in absorption upon addition of a sodium ion is largely an effect of the greater polarization of the azide group by the remotely located ion. The shift to higher frequency is about the magnitude and in the same direction as the experimental outcome for **3c**. The symmetric stretch is much more strongly coupled to other skeletal modes, and the bands are predicted to be at 1332 and 1341  $\text{cm}^{-1}$ , for the free and complexed species, respectively.

Further for **3c**, new absorptions appeared at 2066  $\text{cm}^{-1}$ , 2056  $\text{cm}^{-1}$  and 2055  $\text{cm}^{-1}$ , respectively for the NaSCN-, KSCN- and CsSCN-containing solutions. These latter bands are in the region expected for the CN stretch of the thiocyanate ion [37] in the presence of crown ethers. The spectrum of NaSCN in the presence of 18-crown-6 in THF has been shown to provide a strong, symmetrical band at 2060  $\text{cm}^{-1}$  that has been assigned to the  $\nu_{\text{CN}}$  bands in Nacrown<sup>+</sup>-to-SCN<sup>-</sup> contact ion pairs [38]. To further confirm our assignments, the spectra of the precursor 4-bromo-2-methoxy-1,3-xylyl-18-crown-5 were obtained in the presence and absence of the same salts using the same procedures. Symmetrical bands were observed at 2065  $\text{cm}^{-1}$ , 2056  $\text{cm}^{-1}$  and 2055  $\text{cm}^{-1}$  confirming the origin of the additional bands as CN stretches rather than from, for example, Fermi resonance effects. The origin of the differences in the energies of this band could be complex. The marked decrease from Na<sup>+</sup> to K<sup>+</sup> does not follow the ability of the crown rings to complex these ions which has been shown to be K<sup>+</sup> > Cs<sup>+</sup> > Na<sup>+</sup> [39]. This order was determined for **3c** with a hydrogen in the four position, and the log *K* values were determined to be 3.52(2), 2.76(2) and 2.30(2) by way of a calorimetric titration procedure in methanol. It is possible that the trend in the CN stretching vibrations is the result of the differences in the ion-to-NCS interaction which could be the strongest for Na<sup>+</sup> because the charge density

of this ion is the highest. What has been previously observed is that the CN stretches in free thiocyanates as from R<sub>4</sub>N<sup>+</sup>SCN<sup>-</sup> appear at 2055  $\text{cm}^{-1}$ , and that when ion paired that band shifts to higher frequencies [40].

#### X-ray Diffraction Study.

The ORTEP diagram of **3c** is shown in Figure 1, and selected crystallographic data, bond distances, angles and torsion angles are presented in Tables 1-4. As shown in

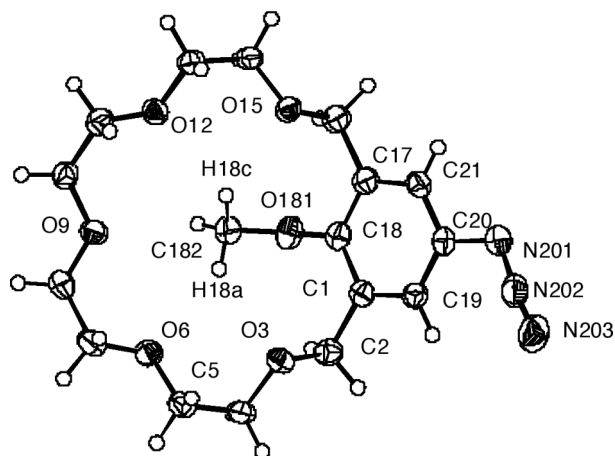


Figure 1. Ortep Drawing of **3c**.

Tables 2 and 3, the bond distances and angles are all in the ranges expected. As with **1**, the N<sub>3</sub> group deviates slightly from linearity with a N201-N202-N203 angle of 173.4(2)°. Also, the mean plane of the N<sub>3</sub> group is about 10.0° out of the plane of the phenyl ring with C19-C20-N201-N202 and C21-C20-N201-N202 torsion angles of -10.8(3) and 93.8(2)°, respectively. Further the N<sub>3</sub> group is bent in the same direction relative to the phenyl ring as the crown ring and OCH<sub>3</sub> group. As presented in Table 3, The N201-N202 and N202-N203 distances are 1.245(2) and 1.127(2) Å, respectively. The observed N-N distances indicate that the terminal bond is about 0.1 Å shorter than the internal. In fact, the analysis of 33 fragments in 25 structures from previously reported crystal structures results in average bond distances corresponding to N202-203, N201-N202 and N201-C20 of 1.133(3), 1.233(22) and 1.427(26) Å, respectively, and average bond angles of 173(11)° (NNN) and 115.9(9)° (CNN) [41]. Hence, the observed results for **3c** are in good agreement with previously reported results.

As shown in the ORTEP diagram, a prominent feature is that the crown ether ring is folded over the face of the phenyl ring. The angle between the plane of the phenyl ring carbons and the mean plane defined by the oxygen atoms is 38.9°. This angle similar to those found for diphenylphosphino-1,3-xylyl-18-crown-5 and 1,3-xylyl-

18-crown-5 for which the reported angles are 38.4° and 20.6°, respectively [20,42]. As indicated above, the CH<sub>3</sub> groups in anisole derivatives with one or none *ortho*-positioned substituents are in the same plane as the phenyl ring. For **3c** however, the CH<sub>3</sub> group is rotated out of the plane of the phenyl ring with dihedral angles of 93.81(14)° and -90.54(14)° for C1-C18-O181-C182, and C17-C18-O181-C182, respectively. We previously determined that this was also the case for the CH<sub>3</sub> groups in tris(3,5-dimethyl-4-methoxyphenyl)phosphine with the result that the corresponding CH-C-O-CH<sub>3</sub> dihedral angles averaged 96.0(2)° and -87.3(2)° [43]. Further, as evident from both the dihedral angles and Figure 1, the CH<sub>3</sub> group is bent in the same direction as the crown ring. One apparent outcome from this is that the crown ring is fairly symmetrical and H-18a is 2.502(2) and 2.484(2) Å from O3 and O6, and H-18c is 2.430 and 2.481(2) Å from O15 and O12, respectively. In addition the O3-O15 and O6-O12 distances are 5.409(2) and 5.198(2) Å, respectively. This symmetry is also evident from the dihedral angles presented in Table 4, which indicate that there is an approximate mirror-plane-passing through C20, C18 and O9.

## EXPERIMENTAL

### Materials.

4-Bromophenol, formaldehyde (37 % solution in water), dimethyl sulfate, phosphorus tribromide, sodium hydride (60 % dispersion in mineral oil), tetraethylene glycol (TEG), *n*-butyl lithium (*n*-BuLi, 2.5 M in hexane), *p*-toluenesulfonyl chloride and sodium azide were obtained from Aldrich Chemical Company. Dry tetrahydrofuran (THF) and dichloromethane were obtained from J. T. Baker. Solvents and remaining chemicals were obtained from a variety of commercial sources. The thiocyanate salts were dried for 24 h at 145 °C prior to use in the infrared studies.

### Instrumentation and Methods.

Melting ranges were recorded with a Thomas-Hoover capillary melting point apparatus. IR Spectra were recorded with a Perkin Elmer 1000 spectrometer as solutions in dichloromethane. NMR spectra were recorded on a JEOL Eclipse-400 MHz spectrometer in CDCl<sub>3</sub> with tetramethylsilane as an internal reference. Chromatographic separations were carried out using 40-75 μm silica gel cartridges fixed in a Biotage® apparatus. The elemental analysis was performed by Midwest Microlabs, Ltd, Indianapolis, Indiana.

### Single-Crystal X-ray Diffraction Study of C<sub>17</sub>H<sub>25</sub>N<sub>3</sub>O<sub>6</sub>.

A colorless needle having the approximate dimensions of 0.43 x 0.20 x 0.08 mm was mounted on a glass fiber in a random orientation. Preliminary examination and data collection were performed with Mo Kα radiation (λ = 0.71073 Å) at 150 K on a Nonius KappaCCD equipped with a graphite crystal, incident beam monochromator. Lorentz and polarization constants were

applied. The structure was solved by direct methods using SIR2002 [44]. Hydrogen atoms were included in the refinement, but they were constrained to the carbon atoms to which they were attached. Refinement was performed using SHELX-97 [45].

The data have been deposited with the Cambridge Crystallographic Data Center, and the CCDC number 284147 has been assigned.

### Synthesis.

*p*-Toluenesulfonyl azide [46], 4-Bromo-2,6-bis(bromomethyl)anisole [47] and 4-bromo-2-methoxy-1,3-xylyl-18-crown-5 [20] were prepared as described previously.

### Preparation of 5-Azido-2-methoxy-1,3-xylyl-18-crown-5 (**3c**).

An oven dried 250 mL three-necked flask was fitted with a magnetic stirrer and filled with argon while still warm. 5-Bromo-2-methoxy-1,3-xylyl-18-crown-5 (6.68 g, 0.0165 mol) and 100 mL of dry THF were added to the flask which was cooled to *ca.* -80 °C using an ethyl acetate and liquid nitrogen slush. *n*-BuLi (6.7 mL, 0.017 mol) was added dropwise over a 15 min period. After the addition was completed, the resulting mixture was stirred for 45 minutes at -80 °C after which *p*-toluenesulfonyl azide (3.29 g, 0.0167 mol) in 20 mL of THF was added dropwise over 20 minutes. After the addition was completed, the resulting mixture was stirred for an additional 5 h at -80 °C. Then the flask was stored in a freezer at -15 °C overnight and then allowed to warm. When the temperature reached 5 °C, the mixture was treated with tetrasodium pyrophosphate decahydrate (7.45 g, 0.0167 mol) dissolved in 15 mL of water. The mixture was stirred for 8 h at 5 °C. The organic layer was separated and collected. An additional 100 mL of water was added to the aqueous layer which was then extracted with 2 x 100 mL of dichloromethane. The organic layers were combined and the solvent was removed *in vacuo* to yield 5.59 g of an orange colored product. A 1.25 gram aliquot of the crude product was purified by chromatography (4% methanol in dichloromethane) to provide 0.60 grams of the desired product. Crystals were obtained by slowly evaporating a solution of the chromatographed solid in a 50:50 mixture dichloromethane and ethyl acetate at -15 °C. mp: 98-100 °C. IR: λ<sub>as</sub> (N=N=N): 2110 (CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 3.4-3.70 (m, 16H), 4.1 (s, 3H), 4.5 (s, 4H), 6.9 (s, 2H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 65.1, 68.7, 68.8, 70.2, 70.7, 122.0, 133.5, 134.4, 156.5.

*Anal.* Calcd for C<sub>17</sub>H<sub>25</sub>N<sub>3</sub>O<sub>6</sub>: C, 55.58 %, H, 6.86 %. Found: C, 55.54%, H, 6.83%.

### Acknowledgment.

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