

Research Article

Synthesis of Diamides and Diimines Derived from 4,4'-(1,3-Phenylenebis(oxy))dianiline, Units for Symmetrical Macrocycles

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4,4'-(1,3-Phenylenebis(oxy))dianiline **1** is an aromatic diamine compound and has been very less utilized in the organic synthesis. Different diimines and diamides were synthesized by reacting compound **1** with aromatic and heterocyclic compounds having different functionalities. These longer electron rich spacer molecules were synthesized to utilize them in the near future in making macrocycles of different sizes and functionalities. A hydrazide was also prepared from a diamide spacer molecule containing ester group. A diamide prepared containing nitrobenzene moiety was further reduced to amine to obtain longer spacer diamine molecule than the starting molecule **1**.

1. Introduction

The condensation of primary amines with carbonyl group was discovered in 1864 by Schiff [1] and has been always the reaction of interest to chemists up to date in the fields of macrocyclic and supramolecular chemistry. The more interesting case is the cyclization of dicarbonyl compounds with diamines which can produce variety of products like [1+1]-condensation, [2+1]-condensation or [1+2]-condensation products, and so forth. These types of reactions lead to macrocyclization after [2+2]-condensation occurs.

The functionally substituted Schiff bases bearing additional donor groups represent the most important class of heteropolydentate ligands in coordination chemistry which can form mono-, bi-, and polynuclear complexes with different transition and nontransition metals. Interest in exploring metal ion complexes with macrocyclic ligands has been continuously increasing owing to the recognition of the role played by these structures in metalloproteins [2]. When synthesizing macrocycles from these unit molecules

being reported, metal ions with different ionic radii and coordination requirements can control the structure and size of the macrocycle [3]. The literature is full of books and reviews devoted to template synthesis of the macrocyclic Schiff-base complexes and their properties [4–10]. Gerbelet et al. analyzed in detail the template synthesis of macrocyclic systems [11] while other reviews of Vigato and coworkers are most comprehensive [12, 13]. Another review focusing on chemistry of pyrrole-containing macrocyclic Schiff bases was published by Callaway et al. [14].

Leading towards different topologically important macrocycles, two different types of macrocycles were the targets. These macrocycles can be electron donors, that is, macrocycles having electron rich heteroatoms and having the donating power to catch or cage the cation inside the ring which can be also used as artificial ion channel for cations in the future. The second type is the acceptor macrocycles, which has electron deficient species and can cage or catch the anions inside the ring or may act as artificial channels for anions. Keeping in mind the aforementioned properties,

different units were synthesized which will lead to these macrocycles. Mainly the three phenyl longer compound 4,4'-(1,3-phenylenebis(oxy))dianiline **1** (Figure 1) was used to synthesize these units having hydrogen bonding interactions.

The molecule **1** is a diamine, electron rich, dinucleophile, easily reacts with acyl halides, aldehyde, and other groups containing electrophilic carbons or good leaving groups. Different units synthesized from **1** and some other molecules are described below.

For the synthesis of donor macrocycles, many units were synthesized which can be used as electrophiles or nucleophile. These groups will be used in different combinations to make macrocycles. These units can be divided into three subgroups according to the functional groups they have, for example, amides, imines, and other units.

2. Result and Discussion

2.1. Amide Units. Different units containing amide bond were synthesized by reacting acyl halides and esters with diamine **1**. Amide units synthesized from acyl chlorides were easy to give amide containing compounds as compared to esters. In a typical reaction, 2.2 molar benzoyl chloride **2** was added dropwise at 0°C to 1 molar diamine **1** solution in dichloromethane in the presence of dry potassium carbonate and stirred until the reaction mixture reached to room temperature. Precipitates were started to develop after the mixture was poured in distilled water which were filtered, and washed with excess of water to remove acids and potassium carbonate. The crude compound **3** was dried in vacuum and characterized through for NMR and other analytical techniques. A general reaction of amide unit formation is given in Scheme 1.

The ¹H NMR showed all the peaks in the spectrum which were expected. The spectrum showed a doublet of doublet at δ 7.86 of four protons, a singlet of two protons at δ 7.83, a doublet of doublet at δ 7.6 of four protons, a doublet of doublet at δ 7.53 of two protons, a doublet of doublet at δ 7.49 of four protons, a triplet of one proton at δ 7.45, a doublet of four protons at δ 7.05, a doublet of doublet of two protons at δ 6.72, and a triplet of one proton at δ 6.62. The UV-visible spectrum was recorded of the product in DMSO and three λ_{max} peaks were observed at 202, 224, and 275 nm with absorbance of 1.51, 0.5, and 0.5, respectively. IR was recorded in KBr disc and the main stretchings observed were 3293 broad, 1646, 1511, 1215, and 693 ν cm⁻¹.

Some amides were also synthesized from esters by refluxing esters in methanol with the diamine **1**. In a model example, an excess amount of di-*tert*-butyl oxalate **4** was refluxed in a methanol with **1** and the reaction progress was monitored with TLC. It took approximately 36 hours to complete the reaction. The crude mixture was purified through column chromatography and the product **5** was analyzed through NMR and EI-MS. The reaction is represented in Scheme 2.

The ¹H NMR of the product was obtained in deuterated chloroform. The peaks observed in the spectrum are a singlet of two protons at δ 9.96, a doublet of four protons at δ

7.95, a triplet of one proton at δ 7.72, a doublet of four protons at δ 7.62, a triplet of one proton at δ 7.2, a doublet of doublet of two protons at δ 6.5, and a singlet of 18 protons belongs to butyl group at δ 1.23. The UV-visible spectrum was obtained in chloroform and the λ_{max} in the spectrum were observed at 227 and 242 nm with absorbencies of 3.927 and 4.0, respectively. The IR spectrum was obtained in KBr disc and the main stretching bands observed were 3727, 2921, 1679, 1587, 1424, 755, and 675 ν cm⁻¹.

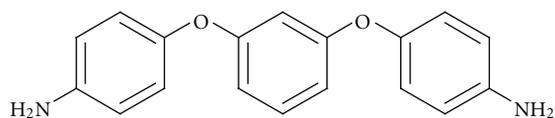
Mainly the amides synthesized from acyl chlorides were obtained in good yield and were pure enough for NMR and no need was felt for purification by chromatography. According to the same procedures described for the synthesis of amide units for macrocycles, other amide units were synthesized which can be used for the synthesis of hydrogen bonding macrocycles directly or after certain reaction(s). Figure 2 shows the examples of amides (**3**, **5–9**) synthesized from the diamine **1**.

All of the above amide units are important for the synthesis of macrocycles which would be having hydrogen bonding properties. Compound **3** has only phenyl rings as benzoyl chloride was used to synthesize it and optimize the reaction conditions and to solve the solubility problems. Compound **6** has –OCH₃ groups which can be demethylated by using BBr₃ to obtain –OH groups. These –OH groups can be further utilized to attach with other longer units having electrophiles, for example, **8** to obtain macrocycles having propyl amide ethers. Compound **8** can also be used to synthesize macrocycles by reacting it with other dinucleophiles to obtain symmetrical and asymmetrical macrocycles. **5** and **9** are both diketones with amide and ester groups but **5** has a bulky butyl group and can be used at high temperature to induce selectivity while **9** is simple methoxy ester and easily convertible to amides or thioesters, and so forth.

Compound **7** has –NO₂ functional groups which cannot be utilized as nucleophiles for the synthesis of macrocycles. The nitro group of the diamide **7** was reduced to obtain again diamine **10** with longer length and with more flexibility and degrees of freedom. Compound **7** was refluxed in acidic ethanol in the presence of Tin(II) chloride as shown in Scheme 3.

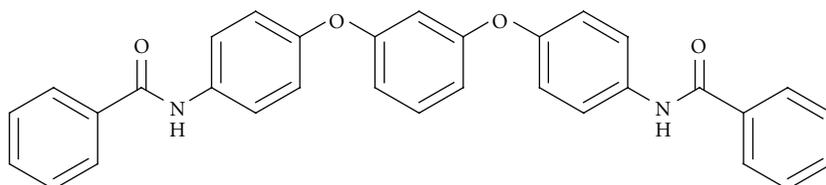
After completion of the reaction, the product was poured in distilled water and neutralized to pH 7. The precipitates formed were filtered and washed further with distilled water. The crude product was purified on column chromatography by using chloroform and methanol as eluent. The product was analyzed by NMR and EI-MS which confirm the formation of the reduced product **1**.

As **5** and **9** are both electrophilic for the synthesis of macrocycles and having esters functionalities. They can be easily converted to hydrazides by reacting it with hydrazine, so they will be acting like nucleophiles for the synthesis of macrocycles and also with more hydrogen bonding properties. The synthesis of dihydrazide **11** was achieved with the help of **5** and **9**. Reactant ester was taken in a test tube and stirred at 0°C for 10 minutes in hydrazine as shown in Scheme 4 and allowed for ten minutes in order to get precipitates.

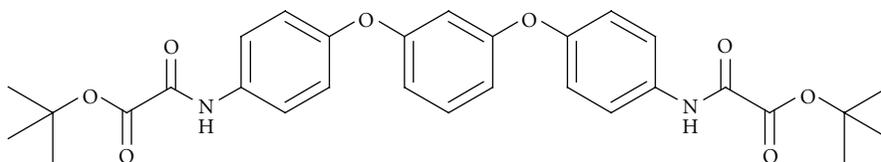


1

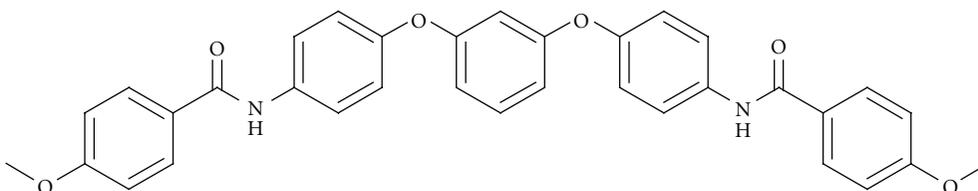
FIGURE 1: Diamine 1.



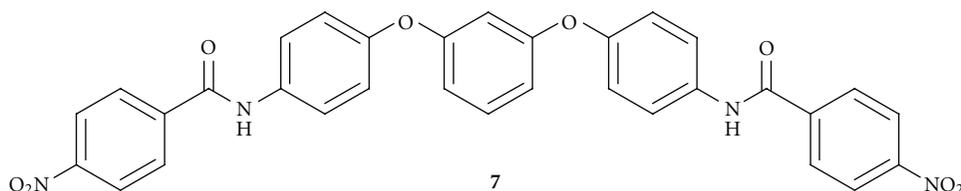
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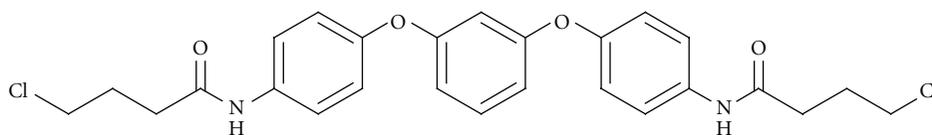
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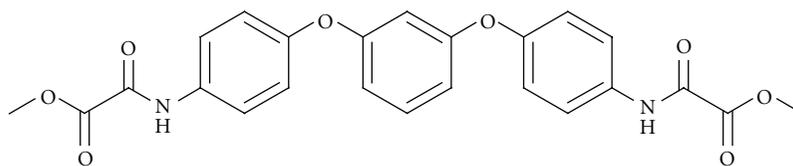
6



7



8



9

FIGURE 2: Different diamide units from diamine 1.

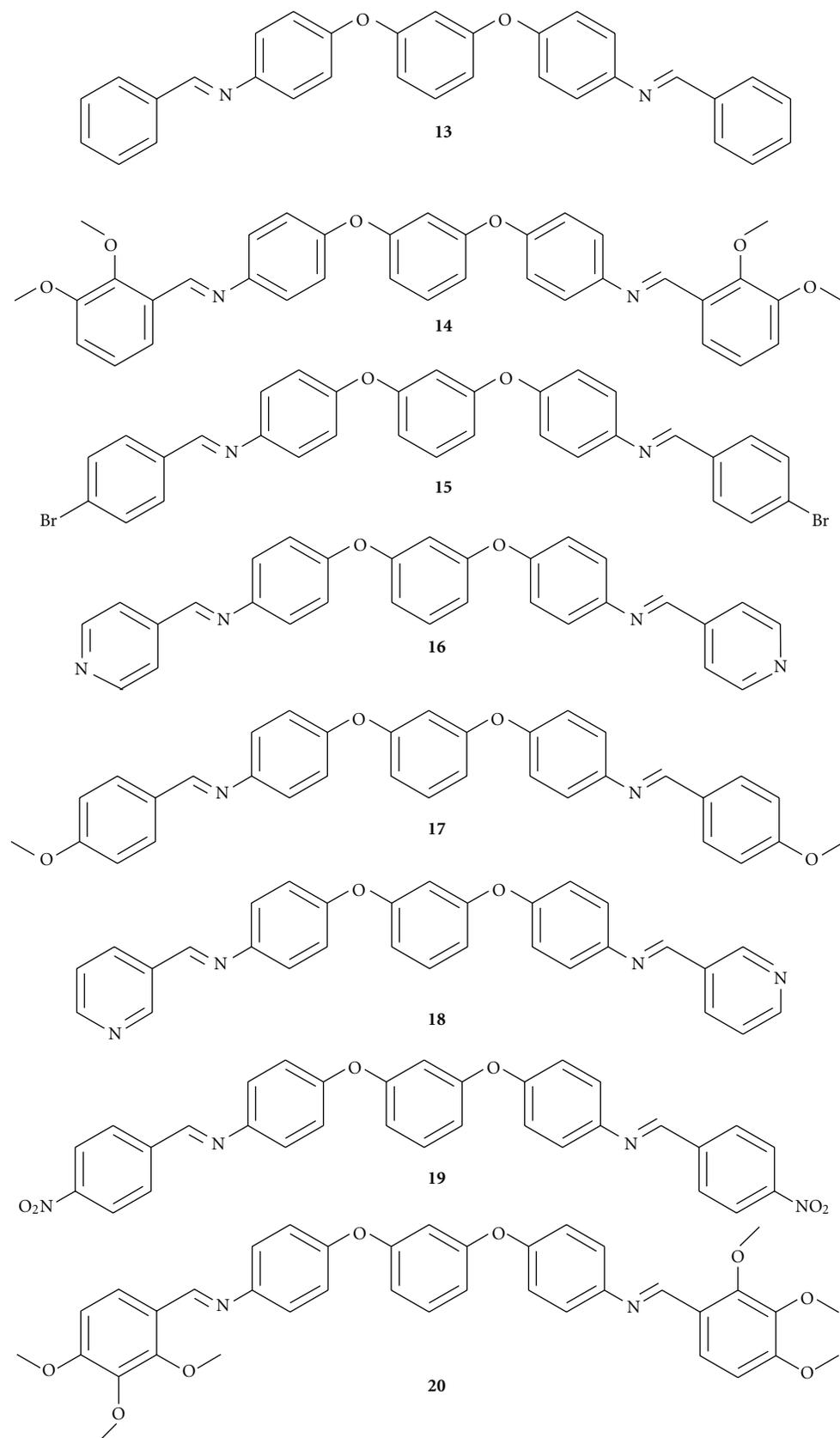
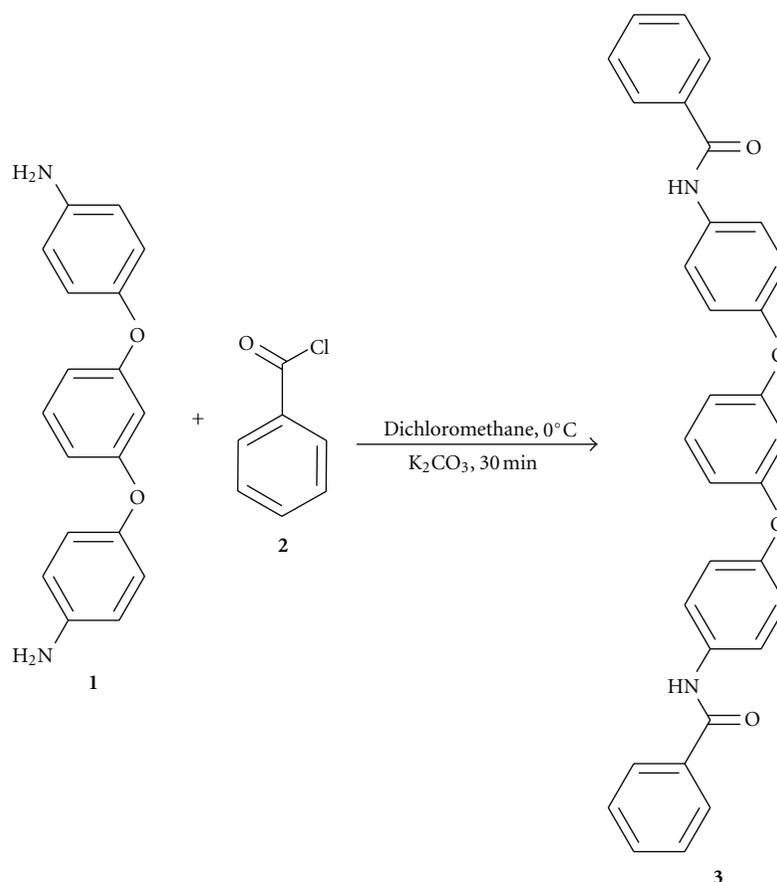


FIGURE 3: Different diimine units from diamine 1.



SCHEME 1: Synthesis of spacer diamide unit from acyl chloride.

White pasty precipitates were obtained, which were filtered and washed with cold distilled water to remove extra hydrazine. The crude product was obtained as white jelly, which solidified after two days to form a white solid.

The compound was characterized through for ¹H NMR in dimethyl sulfoxide and showed two singlet of two protons at δ 10.6 and 10.2, two doublets of four protons at δ 7.8 and 7.0, two triplets, each of one proton at δ 7.3 and 6.5, a doublet of doublet of two protons at δ 6.6, and a broad peak of four protons at δ 4.6. The UV-visible spectrum was recorded in DMSO and two λ_{max} peaks were observed at 380 and 330 nm having absorbencies of 1.56 and 0.28. The IR in KBr was also obtained and the main stretchings were 3284, 1658, 1513, 1217, and 541 ν cm⁻¹.

2.2. Imine Units. After synthesizing the longer units for the synthesis of macrocycles having hydrogen bonding properties, another motif (imine) was selected, this could impart unsaturation and conjugation to the macrocycles. Similar to these motifs (imine) also provide suitable functional group for electrophilic substitution reaction. The starting molecule 1 is a diamine and it would be very easy to react it with aldehydes to obtain imine units. As imines are also having good interactions for hydrogen bonding, these imine units could be directly utilized for the synthesis of

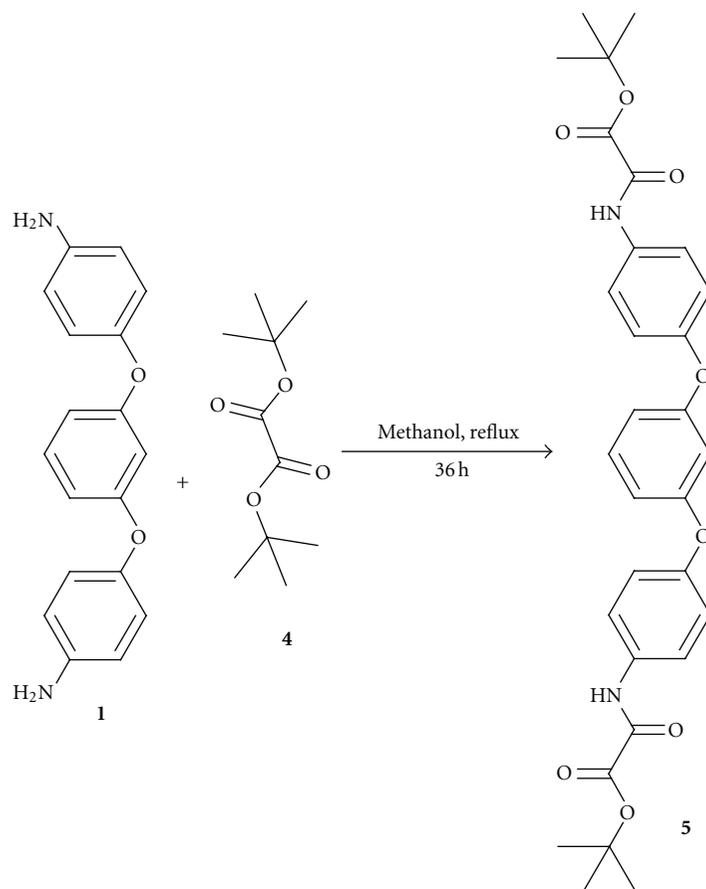
macrocycles or can be reduced in the next step to secondary amines. Both imine and amine containing macrocycles are important for the preparation of nanotubes because of their supramolecular interactions of N–H–N bonds.

In a typical reaction, the diamine 1 was condensed with benzaldehyde 12 in dichloromethane at room temperature to form imine 13 as shown in Scheme 5.

The reaction was completed in one hour. The solvent was evaporated and yellow crystalline material was obtained which was purified by recrystallization from ethanol. The product 13 was characterized through ¹H NMR and EI-MS to confirm the product formation. The ¹H NMR showed a sharp singlet showing the presence of imine proton, and also the IR spectra showed C=N stretching and bending peaks.

Other longer imine units were synthesized which would be used directly or after reducing for the synthesis of longer units and macrocycles. The imine units (13–20) synthesized from diamine 1 are shown in Figure 3.

The product 13 was obtained in one hour at room temperature in DCM. The 13 was selected for further condensation with aldehyde and ketone to induce further spacer elongation. The imines having one or more –OCH₃ groups, for example, 17, 14, and 20 can be first reduced to secondary amines and then demethylate by using BBr₃ in dichloromethane to obtain –OH groups. These units would be



SCHEME 2: Synthesis of spacer diamide unit from esters.

having both R–NH–R and –OH groups which would be used for introduction of functional groups or substitutions. The bromo-derivative imine unit **15** is suitable for Sonogashira coupling reaction [15] for the synthesis of macrocycle which would be having properties of acetylene and imine (or amine if reduced before Sonogashira coupling reaction). The imine unit **19** has –NO₂ group which can be reduced to –NH₂ groups and further longer chains would be obtained having nucleophilic properties of amines, which could be reacted with ester amine **9** synthesized before to obtain macrocycles having different properties.

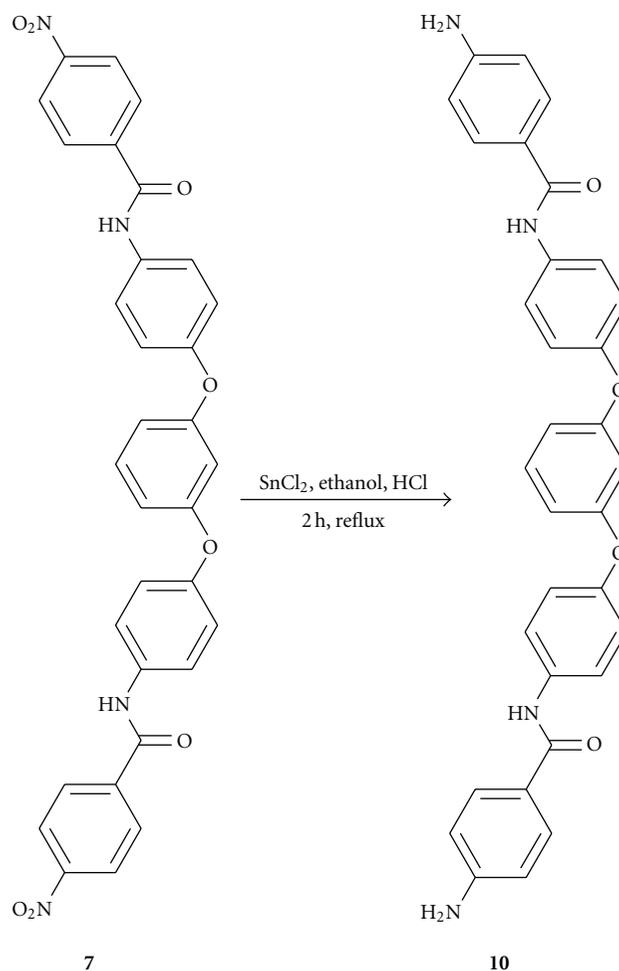
Most of these imine units synthesized were obtained in the form of yellow crystalline material, so the –OCH₃ imine unit **17** was subjected to X-ray crystallography and nice crystallographic structure was obtained from the study which was also a source of confirmation of the product [16].

Most of the above synthesized units are electron rich and would be used in the synthesis of electron rich macrocycles. Certain imine units were also synthesized which would be used in the future for the synthesis of electron rich macrocycles, for example, **16** and **18**. These two imine units consist of pyridine rings which could be easily used as nucleophile and will result electron deficient macrocycles which would attract any electron rich molecule towards its center because of the supramolecular attractions.

3. Experimental

All the reactions were performed according to standard methods with clean glassware and from commercial chemicals which were ultrapure. The work up of different reactions was performed by different procedures according to the need and type of reaction. Compounds were purified by column chromatography using column and flash silica, and recrystallization with different solvents. Some reactions are same except the chemicals reacted, so instead writing all of them, a model reaction will be written. Characterization of pure compounds was done by different techniques including Mass Spectrometric techniques, that is, EIMS (JEOL JMS600), FAB+, FAB–; ¹HNMR (Bruker Avance 400, Avance AV 300), UV (SECOMAM, ANTHJRPC V. 4.1 h), IR (VECTOR22), and TLC. The procedures of the compounds synthesized are given below.

N,N'-(4,4'-(1,3-phenylenebis(oxy))bis(4,1-phenylene))bis(4-chlorobutanamide) (**8**). A representative reaction for amide synthesis is given here for **8**, otherwise the difference in procedure is given in the experimental if any. 100 mg (0.342 mmol) of 4,4'-(1,3-phenylenebis(oxy))dianiline **1** was dissolved in 2 mL dichloromethane in a dry test tube with stirring and cold at 0 °C. K₂CO₃ was added to neutralize



SCHEME 3: Reduction of diamide-nitro unit to diamide-amine spacer molecule.

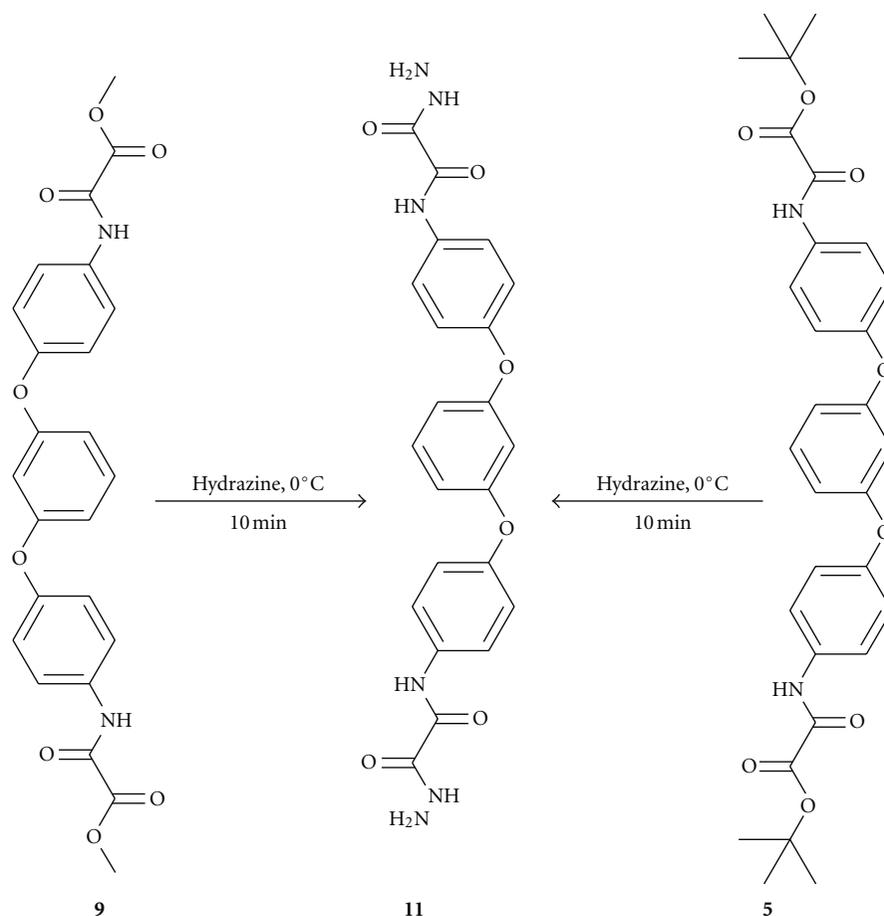
HCl. Few drops of 4-chlorobutanoyl chloride were added in portions to reaction mixture. At room temperature, the reaction mixture was poured in distilled water. The desired compound **8** was precipitated in water. The target molecule was filtered and washed with distilled water and dried, obtained as cream color solid. EIMS m/z : 501; $^1\text{H NMR}$ 400 MHz, DMSO-d_6 δ (ppm): 9.99 (s, 2H), 7.61 (d, 4H, $J = 8.7$ Hz), 7.29 (t, 1H, $J = 8.1$ Hz), 7.01 (d, 4H, $J = 8.7$ Hz), 6.6 (dd, 2H, $4J = 2.4$ Hz, $3J = 8.4$ Hz), 6.5 (t, 1H, $4J = 2.1$ Hz), 3.67 (t, 4H, $J = 6.6$ Hz), 2.46 (t, 4H, $J = 7.2$ Hz), 2.02 (quint, 4H, $J = 6.9$ Hz); UV DMSO λ_{max} nm (abs): 271 (1.68); IR KBr $\nu \text{ cm}^{-1}$: 3291, 1656, 1512, 1228, 851; Anal. Calculated $\text{C}_{26}\text{H}_{26}\text{Cl}_2\text{N}_2\text{O}_4$ (501.40): C, 62.28; H, 5.23; N, 5.59; found: C, 63.561; H, 3.701; N, 6.137.

N,N'-(4,4'-(1,3-phenylenebis(oxy))bis(4,1-phenylene))dibenzamide (**3**). Benzoly chloride was added according to the previous procedures, and the desired compound was obtained as white solid, purified using ethanol as eluent in column chromatography, obtained as white crystals; EIMS m/z : 500; $^1\text{H NMR}$ 400 MHz, CDCl_3 δ (ppm): 7.86 (d, 4H, $J = 8.4$ Hz), 7.78 (s, 2H, -NH), 7.60 (d, 4H, $J = 8.90$ Hz),

7.53 (d, 2H, $J = 7.1$ Hz), 7.49 (d, 4H, $J = 7.5$ Hz), 7.45 (t, 1H), 7.05 (d, 4H, $J = 8.88$ Hz), 6.72 (dd, 2H, $4J = 2.31$ Hz, $3J = 8.22$ Hz), 6.62 (t, 1H, $J = 2.26$ Hz); UV DMSO λ_{max} nm (abs): 202 (1.53), 224 (0.5), 275 (0.5); IR KBr $\nu \text{ cm}^{-1}$: 3293 broad, 1646, 1511, 1215, 693.

t-Butyl-2,2'-(4,4'-(1,3-phenylenebis(oxy))bis(4,1-phenylene))bis(azanediyl)bis(2-oxoacetate) (**5**). 100 mg of **1** was dissolved in 3 mL methanol di-*t*-butyl oxalate was added in excess, and refluxed for 36 hours, evaporated and purified by ethanol as eluent in column chromatography, obtained as brownish solid; EIMS m/z : 548; $^1\text{H NMR}$ 400 MHz, CDCl_3 δ (ppm): 9.96 (s, 2H, -NH), 7.95 (d, 4H, $J = 8.45$ Hz), 7.72 (t, 1H, $J = 10.7$ Hz), 7.62 (d, 4H, $J = 8.48$ Hz), 7.2 (t, 1H), 6.5 dd (2H), 1.64 (br, s, 18H); UV CDCl_3 λ_{max} nm (abs): 227 (3.927), 242 (4.0); IR KBr $\nu \text{ cm}^{-1}$: 3727, 2921, 1679, 1587, 1424, 755, 675.

N,N'-(4,4'-(1,3-phenylenebis(oxy))bis(4,1-phenylene))bis(4-methoxybenzamide) (**6**). The desired compound was obtained by the coupling of **1** and anisoyl chloride according to earlier procedure; EIMS m/z : 560; $^1\text{H NMR}$ 400 MHz,

SCHEME 4: Synthesis of dihydrazide from esters **9** and **5**.

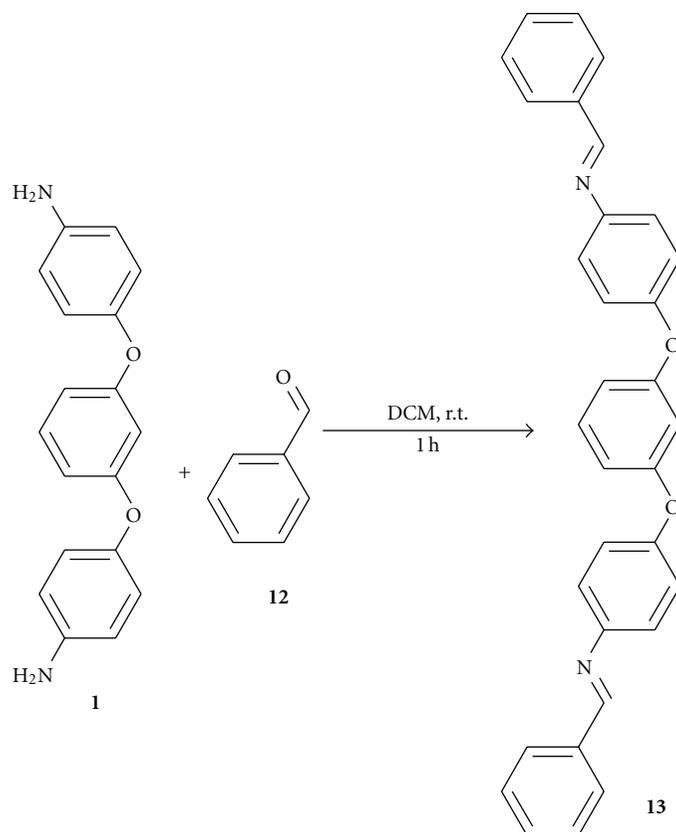
DMSO_d δ (ppm): 10.11 (s, 2H, -NH), 7.95 (d, 4H, *J* = 8.63 Hz), 7.89 (d, 4H, *J* = 8.69 Hz), 7.79 (d, 4H, *J* = 8.86 Hz), 7.3 (t, 1H, *J* = 8.20 Hz), 6.99 (d, 4H, *J* = 8.7 Hz), 6.69 (dd, 2H, 4*J* = 2.00 Hz, 3*J* = 8.22 Hz), 6.5 (t, 1H), 3.83 (d, 6H, *J* = 4.29 Hz); UV DMSO λ_{max} nm (abs): 274 (1.87), 203 (0.262); IR KBr ν cm⁻¹: 3329 broad, 3419, 2840, 1650, 1604, 1508, 1258, 838; Anal. Calculated for: C₃₄H₂₈N₂O₆ (560.60), Elemental Analysis: C, 72.84; H, 5.03; N, 5.00; O, 17.12, Found: C, 64.50; H, 4.95; N, 4.836.

N,N'-(4,4'-(1,3-phenylenebis(oxy))bis(4,1-phenylene))bis(4-nitrobenzamide) (**7**). To a cooled solution of **1** in dichloromethane, 4-nitrobenzoyl chloride was added dropwise, yellow solid was obtained, purified by column chromatography using hexane and ethyl acetate as eluent, obtained as bright yellow solid; EIMS *m/z*: 590; ¹H NMR 400 MHz, DMSO_d δ (ppm): 10.60 (s, 2H, -NH), 8.37 (d, 4H, *J* = 8.69 Hz), 8.18 (d, 4H, *J* = 8.68 Hz), 7.81 (d, 4H, *J* = 8.85 Hz), 7.35 (t, 1H, *J* = 8.12 Hz), 7.11 (d, 4H, *J* = 8.92 Hz), 6.73 (dd, 2H, 4*J* = 2.2 Hz, 3*J* = 8.15 Hz), 6.58 (t, 1H, *J* = 2.07 Hz); UV DMSO λ_{max} nm (abs): 203 (2.613), 255 (2.105); IR KBr ν cm⁻¹: 3777, 3698, 3319 broad, 3115, 2879, 2828, 1814, 1762, 1718, 1591, 1322, 712; Anal. Calculated:

C₃₂H₂₂N₄O₈ (590.54): C, 65.08; H, 3.75; N, 9.49; O, 21.67; found: C, 54.665; H, 3.625; N, 8.216.

Dimethyl-2,2'-(4,4'-(1,3-phenylenebis(oxy))bis(4,1-phenylene)) bis(azanediyl)bis(2-oxoacetate) (**9**). Few drops of methyl 2-chloro-2-oxoacetate were added to **1**, and desired compound was obtained as white solid according to the earlier procedure; EIMS *m/z*: 464; ¹H NMR 400 MHz, DMSO_d δ (ppm): 10.85 (s, 2H), 7.77 (d, 4H, *J* = 9.2 Hz), 7.3 (t, 1H, *J* = 8.4 Hz), 7.08 (d, 4H, *J* = 8.8 Hz), 6.70 (dd, 2H, 4*J* = 2.4 Hz, 3*J* = 8.4 Hz), 6.5 (t, 1H, *J* = 2.4 Hz), 3.84 (s, 6H, -OCH₃); UV DMSO λ_{max} nm (abs): 288; IR KBr ν cm⁻¹: 3336, 1694, 1543, 1214, 853, 690, 494; Anal. Calculated: C₂₄H₂₀N₂O₈ (464.42); C, 62.07; H, 4.34; N, 6.03; O, 27.56; found: C, 62.933; H, 4.346; N, 6.238.

N,N'-(4,4'-(1,3-phenylenebis(oxy))bis(4,1-phenylene))bis(4-aminobenzamide) (**10**). 100 mg **7** was taken in 4 mL of ethanol and 250 mg SnCl₂ was added. Few drops of concentrated HCl were also added. Refluxed for 4 hours and poured in 100 mL of distilled water. Extracted with ethyl acetate and obtained as brown solid, purified on column chromatography using 1:1 chloroform:methanol as eluent; EIMS *m/z*:



SCHEME 5: Synthesis of diimine unit from benzaldehyde.

530; $^1\text{H NMR}$ 400 MHz, CDCl_3 δ (ppm): 8.1 (s, 2H, $-\text{NH}$), 7.70 (d, 4H, $J = 8.51$ Hz), 7.67 (d, 4H, $J = 7.9$ Hz), 7.57 (d, 4H, $J = 8.83$ Hz), 7.19 (t, 1H), 7.03 (d, 4H, $J = 8.82$ Hz), 6.70 (dd, 2H, $J = 4.07$ Hz), 6.60 (t, 1H, $J = 2.52$ Hz), 4.00 (s, 4H, $-\text{NH}_2$); UV CDCl_3 λ_{max} nm (abs): 203 (1.55), 300 (0.979); IR KBr ν cm^{-1} : 3780, 3697, 3464, 3349 broad, 2922, 2854, 1725, 1600, 1262, 1210, 1117, 838, 677.

N,N'-(4,4'-(1,3-phenylenebis(oxy))bis(4,1-phenylene))bis(2-hydrazinyl-2-oxoacetamide) (**11**). 100 mg of **9/5** was taken in a test tube and stirred at 0°C for 10 minutes in hydrazine, a white paste was obtained, which was filtered washed with cooled distilled water to remove extra hydrazine, dried and obtained as white jelly, which was solidified after two days in the form of a white solid; EIMS m/z : 464; $^1\text{H NMR}$ 400 MHz, DMSO-d_6 δ (ppm): 10.64 (s, 2H, $-\text{NH}-$), 10.25 (br, s, 2H, $-\text{NH}-$), 7.84 (d, 4H, $J = 9$ Hz), 7.32 (t, 1H, $J = 8.4$ Hz), 7.06 (d, 4H, $J = 9$ Hz), 6.68 (dd, 2H, $4J = 2.4$ Hz, $3J = 8.4$ Hz), 6.5 (t, 1H, $J = 2.1$ Hz), 4.61 (br, s, 4H, $-\text{NH}_2$); UV DMSO λ_{max} nm (abs): 380 (1.56), 330 (0.28); IR KBr ν cm^{-1} : 3284, 1658, 1513, 1217, 541.

N,N'-(4,4'-(1,3-phenylenebis(oxy))bis(*N*-benzylideneaniline) (**13**). One representative reaction of imine synthesis is given for **13**, other imines were synthesized according to the same procedure, and otherwise difference is given in the experimental.

100 mg (0.342 mmol) of 4,4'-(1,3-phenylenebis(oxy))dianiline **1** dissolved in 2 mL DCM in test tube, and few drops of benzaldehyde were added, stirred for 30 minutes at 35°C . The solvent of reaction mixture was evaporated under reduced pressure and purified by column chromatography using DCM as eluent, recrystallized in DCM. White crystals were obtained in 81% yield. EIMS m/z : 468; $^1\text{H NMR}$ 400 MHz, CDCl_3 δ (ppm): 8.46 s (2H), 7.91 (m, 4H), 7.5 (m, 6H), 7.28 (m, 2H), 7.2 (d, 4H, $J = 9$ Hz), 7.0 (d, 4H, $J = 9$ Hz), 6.8 (m, 2H); UV CHCl_3 λ_{max} nm (abs): 250 (2.0), 308 (3.5), 350 (3.5); IR KBr ν cm^{-1} : 3408 broad, 3061, 2876, 1623, 1585; Anal. Calculated for $\text{C}_{32}\text{H}_{24}\text{N}_2\text{O}_2$ (468.55): C, 82.03; H, 5.16; N, 5.98; O, 6.83. Found C, 75.90; H, 5.06; N, 6.01.

N,N'-(4,4'-(1,3-phenylenebis(oxy))bis(*N*-(2,3-dimethoxybenzylidene)aniline) (**14**). Obtained as brownish yellow solid and crystallized out from dichloromethane; EIMS m/z $\text{C}_{36}\text{H}_{32}\text{N}_2\text{O}_6$: 588; $^1\text{H NMR}$ 400 MHz, CDCl_3 δ (ppm): 8.85 (s, 2H), 7.73 (d, 2H, $J = 7.8$ Hz), 7.07 d (4H), 7.21 d (4H), 7.12 (t, 2H, $J = 8.02$ Hz), 7.06 (d, 2H, $J = 8.54$ Hz), 7.02 (d, 2H, $J = 8.19$ Hz), 6.73 (dd, 2H, $J = 6.19$ Hz), 6.70 (t, 1H), 3.90 (s, 6H), 3.89 (s, 6H).

N,N'-(4,4'-(1,3-phenylenebis(oxy))bis(*N*-(4-bromobenzylidene)aniline) (**15**). Obtained as light yellow solid and crystallized out from dichloromethane as light yellow crystals, EIMS m/z : 626; $^1\text{H NMR}$ 400 MHz, CDCl_3 δ

(ppm): 8.4 (s, 2H), 7.8 (d, 4H, $J = 8.4$ Hz), 7.6 (d, 4H, $J = 8.38$ Hz), 7.23 (d, 4H, $J = 8.81$ Hz), 7.0 (d, 4H, $J = 8.8$ Hz), 6.8 (dd, 2H, $4J = 2.19$ Hz, $3J = 8.15$ Hz), 6.7 (t, 1H, $J = 2.1$ Hz); UV CHCl₃ λ_{\max} nm (abs): 222 (3.87), 259 (3.7), 326 (0.6); IR KBr ν cm⁻¹: 3449 broad, 2873, 1680, 1616, 1586, 1496, 1237, 852, 532; Anal. Calculated for: Chemical Formula: C₃₂H₂₂Br₂N₂O₂ (626.34): C, 61.36; H, 3.54; Br, 25.51; N, 4.47; O, 5.11 Found C, 58.73; H, 3.541; N, 4.7.

(*N,N'*)-4,4'-(1,3-phenylenebis(oxy))bis(*N*-(pyridin-4-ylmethylene) aniline) (**16**). Synthesized as **13**, yellow crystals obtained. EIMS m/z : 470; ¹H NMR 400 MHz, CDCl₃ δ (ppm): 8.75 (d, 4H, $J = 5.88$ Hz), 8.46 (s, 2H), 7.73 (d, 4H, $J = 5.88$ Hz), 7.30 (d, 4H, $3J = 8.76$ Hz), 7.09 (d, 4H, $J = 8.76$ Hz), 6.78 (dd, 2H, $4J = 2.28$ Hz, $3J = 8.17$ Hz), 6.72 (t, 1H, $4J = 2.1$ Hz); UV CHCl₃ λ_{\max} nm (abs): 416 (0.218); IR KBr ν cm⁻¹: 3727, 3432 broad, 1586, 1478; Anal. Calculated for C₃₀H₂₂N₄O₂ (470.17): C, 76.58; H, 4.71; N, 11.91; O, 6.80. Found C, 64.83; H, 4.43; N, 10.15.

(*N,N'*)-4,4'-(1,3-phenylenebis(oxy))bis(*N*-(4-methoxybenzylidene)aniline) (**17**). Obtained as brownish crystalline solid and XRD [16] analysis were conducted; EIMS m/z : 528; ¹H NMR 400 MHz, CDCl₃ δ (ppm): 8.38 (s, 2H), 7.84 (d, 4H, $J = 8.66$ Hz), 7.2 (d, 4H, $J = 8.71$ Hz), 7.05 (d, 4H, $J = 8.70$ Hz), 6.98 (d, 4H, $J = 8.66$ Hz), 6.73 (dd, 2H, $4J = 2.1$ Hz, $3J = 10.2$ Hz), 6.69 (t, 1H), 3.86 (s, 6H, -OCH₃); UV CHCl₃ λ_{\max} nm (abs): 242 (0.08); IR KBr ν cm⁻¹: 3729, 2958, 2839, 1685, 1602, 1507, 1253; Anal. Calculated for: C₃₄H₂₈N₂O₄ (528.20): C, 77.25; H, 5.34; N, 5.30; O, 12.11; Found C, 73.26; H, 5.32; N, 5.38.

(*N,N'*)-4,4'-(1,3-phenylenebis(oxy))bis(*N*-(4-nitrobenzylidene)aniline) (**19**). Obtained as red amorphous solid; EIMS m/z : 558; ¹H NMR 400 MHz, CDCl₃ δ (ppm): 8.56 (s, 2H), 8.33 (d, 4H, $J = 8.7$ Hz), 8.01 (d, 4H, $J = 8.7$ Hz), 7.30 (d, 4H, $J = 9$ Hz), 7.09 (d, 4H, $J = 9$ Hz), 6.79 (dd, 2H, $2J = 2.7$ Hz, $3J = 8.1$ Hz), 6.76 (t, 1H, $J = 2.1$ Hz); UV CHCl₃ λ_{\max} nm (abs): 206 (1.53), 264 (1.72); IR KBr ν cm⁻¹: 3452 broad, 3098, 2852, 1900, 1695, 1579, 1504, 1474; Anal. Calculated for C₃₂H₂₂N₄O₆ (558.54): C, 68.81; H, 3.97; N, 10.03; O, 17.19 Found C, 63.52; H, 3.97; N, 9.53.

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