Dicarbamates: Synthesis and substituent effects on the barrier to rotation around the N-CO bond

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(Received: 04 September 2016, accepted: 04 October 2016)

Abstract: A series of dicarbamates have been synthesized by addition of diols to isocyanates. These products were characterized by NMR, IR, and HRMS analyses. Substituent effects on the barrier to rotation around N-CO bond were investigated using variable temperature ^{1}H NMR spectroscopy.

Keywords: Dicarbamates, diols, isocyanates, barrier to rotation, variable temperature ^{1}H NMR.

INTRODUCTION

Carbamates (urethanes) are attracting considerable attention due to their potential scientific and technological applications [1-11]. For instances, they are widely used as raw materials in agrochemicals (pesticides, insecticides and herbicides) [1-4], dyestuffs [5] and pharmaceuticals [6, 7]. In addition, carbamates can be used to increase the abrasion resistance of polyurethane compositions [8], improving the hardness of urethane-based adhesives and sealants and adjusting viscosity values of oils and greases when used as additives [9]. Carbamates with alkyl side chains have potential applications as vehicles in reprography and ink jet printing technologies [10, 11].

Among the different routes of the synthesis of carbamates, the addition of alcohols to isocyanates is the most common method [12-16]. In a previous work in our laboratory, F-alkyl bis(N-aroxy or alkoxysulfonyl)dicarbamates were prepared by the reaction of F-alkyldiols with alkoxy/aroxysulfonyl isocyanates [17]. In a recent work Soto *et al.* have reported on the reaction of fluorinated diols with aryl/alkyl isocyanates to give the corresponding dicarbamates [18].

On the other hand, the presence of C-N bond with a partially double character in carbamates can, in favorable cases, give rise to the two possible *s-cis* and *s-trans* stereoisomers following rotation around this bond [19-24]. In addition, it was generally shown that the pharmacological activity depends on molecular flexibility, which is governed by hindered rotation around chemical bonds as is the case of conjugated C–N linkages in amides, carbamates, thiocarbamates, and related systems [25-29].

In a previous work, we have described the synthesis of bis(thiocarbamates) from the reaction of dithiols with aryl/alkyl isocyanates as well as a conformational study using variable temperature (VT) NMR spectroscopy [30]. Herein, we extend this reaction to diols for the preparation of new dicarbamates. The rotational barriers around the C-N bond in these dicarbamates using VT NMR were measured and compared to those obtained in bis(thiocarbamates) analogues.

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RESULTS AND DISCUSSION

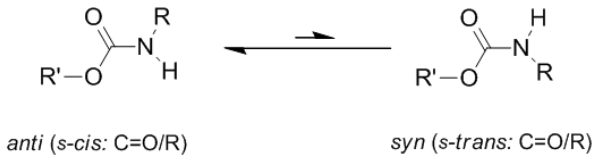
1. Synthesis

The reaction of 1 equiv. of propane-1,3-diol or triethyleneglycol with isocyanates in dry THF at room temperature gave the corresponding dicarbamates **2** and **3** in a 48-86% yield (Table I). They were obtained as white powders which are soluble in a mixture of dimethylsulfoxide (DMSO) and chloroform. It should be noted that compounds **2a, 3a** and **3b** were previously prepared by a different method [31-34]. The synthesized dicarbamates **2** and **3** were fully characterized by IR, (^{1}H and ^{13}C) NMR spectroscopy, and HRMS. The IR spectra show strong band absorptions at about 3300 and 1700-1620 cm^{-1} assigned respectively to the N–H and C=O stretching vibrations. The (^{1}H and ^{13}C) NMR spectra of all dicarbamates show a doubling of signals at room temperature due to the rotation around N-CO bond which results in the presence of two conformational *s-cis* (*anti*) and *s-trans* (*syn*) rotamers with predominance of the *s-cis* (*anti*) form (Fig. 1). This assignment was based on the assumption that secondary carbamates and amides strongly prefer an *s-cis* (*anti*) conformation [35] and on our previous data for bis(thiocarbamates) [30].

The results of Table I show that lengthening the chain between the two carbamate moieties using a longer diol, triethyleneglycol, led to a slight decrease in the reaction yield and a further increase in the proportion of the major isomer (*s-cis vs. s-trans*).

2. NMR study

The duplication of signals observed in the NMR spectra of some dicarbamates (**2** and **3**), at room temperature, is mainly due to the dynamic exchange that occurs between the two conformers *s-cis* and *s-trans* resulting from the rotation around the N-CO bond. This rotational dynamic equilibrium was studied by the method of coalescence using variable temperature ^{1}H NMR in DMSO + $CDCl_3$.



anti (*s-cis:* C=O/R) *syn* (*s-trans:* C=O/R)

(R = alkyl or aryl; R' : remaining of bis(carbamate))

Figure 1: s-cis/s-trans equilibrium for dicarbamates **2** and **3**.

In these dicarbamates (**2** and **3**), the rate constants *kc* were calculated at the coalescence temperature (*Tc*) using the equation ($kc = (\pi \times \Delta\upsilon)/2^{1/2}$)). The peak separation ($\Delta\upsilon$) was obtained from spectra acquired at temperatures well below coalescence. As the system involves an exchange between two unequally populated sites [36], the rate constant k_c calculated by the above equation is therefore the average of the forward (k_1) and reverse (k_{-1}) rate constants. In this case, we used the following approximation formulas most accurate when the molar fractions are between 0.2 and 0.8: $k_1 = (1 + \Delta p)kc$ and $k_{-1} = (1 - \Delta p)kc$ with $\Delta p = p_B - p_A$, the difference in mole of the two species A and B (assuming B is the predominant species) [36]. Considering the transmission coefficient to be unity, the free energies of activation ($\Delta G_1^{\neq}$and $\Delta G_{-1}^{\neq}$) were calculated according to Eyring Eq. (1) together with Eqs. (2) and (3) [37].

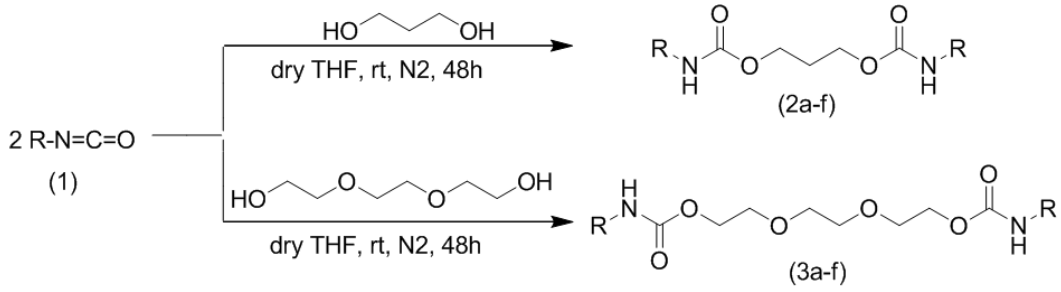
$$k_c = (kT/h) \exp(\Delta G^{\neq}/RT) \quad (1)$$

$$\Delta G_1^{\neq} = 19.14Tc\,(10.32 + \log Tc/k_{1c}) \times 10^{-3} \quad (2)$$

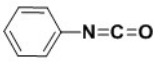
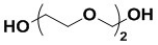
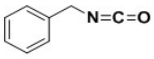
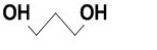
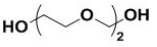
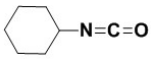
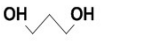
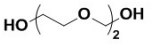
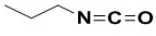
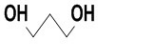
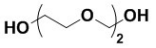
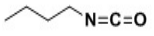
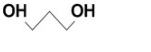
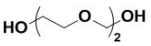
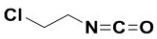
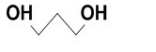
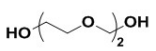
$$\Delta G_{-1}^{\neq} = 19.14Tc\,(10.32 + \log Tc/k_{-1c}) \times 10^{-3} \quad (3)$$

The results of the dynamic ^{1}H NMR study of the dicarbamates **2a-f** thus obtained are shown in Table II which indicates a clear difference in the rotational barrier between the dicarbamates **2a-b** and **2c-f**. In fact, aromatic derivatives **2a** and **2b**, showing a doubling of signals at room temperature, could not be brought to coalescence upon heating even at 358K (Fig. 2) where ($\Delta G_1^{\neq}$and $\Delta G_{-1}^{\neq}$) values are estimated. However, in dicarbamates **2c-f**, the coalescence temperature was reached and in order to slow down the chemical exchange, these samples were cooled below 300 K (Fig. 2). This indicates that, electron-withdrawing N-substituents of phenyl and benzyl (**2a** and **2b**) lead to higher barriers to rotation ($\Delta G_1^{\neq}$and $\Delta G_{-1}^{\neq}$) whilst electron-releasing N-substituents of c-C_6H_{11}, n-Pr, n-Bu and Cl-CH_2-CH_2 (**2c-f**) decrease the barrier to rotation, in agreement with behavior previously observed for their sulfur analogs, bis(thio-carbamates) [30]. The results shown in Tables II and III indicate that the difference in the barrier to rotation between dicarbamate **2a** and **2e** is more important than in dicarbamates **3a** and **3e** which could be explained

Table I: Synthesis of dicarbamates **2a-f** and **3a-f**.



R= Ph ; Bz; c-C_6H_{11} ; n-Pr; n-Bu; Bz; Cl-CH_2-CH_2

Isocyanate	Diol	Bis(carbamate)	Yield (%)	Isomer ratio (%)[a]
		**2a**	86	95:05
		**3a**	84	98:02
		**2b**	79	90:10
		**3b**	71	92:08
		**2c**	73	51:49
		**3c**	68	55:45
		**2d**	84	85:15
		**3d**	75	91:09
		**2e**	76	79:21
		**3e**	69	93:07
		**2f**	52	90:10
		**3f**	48	91:09

a: Approximate *s-cis/s-trans* ratio measured at room temperature from integration of NH NMR signals in $CDCl_3$/DMSO-d_6 (80:20)

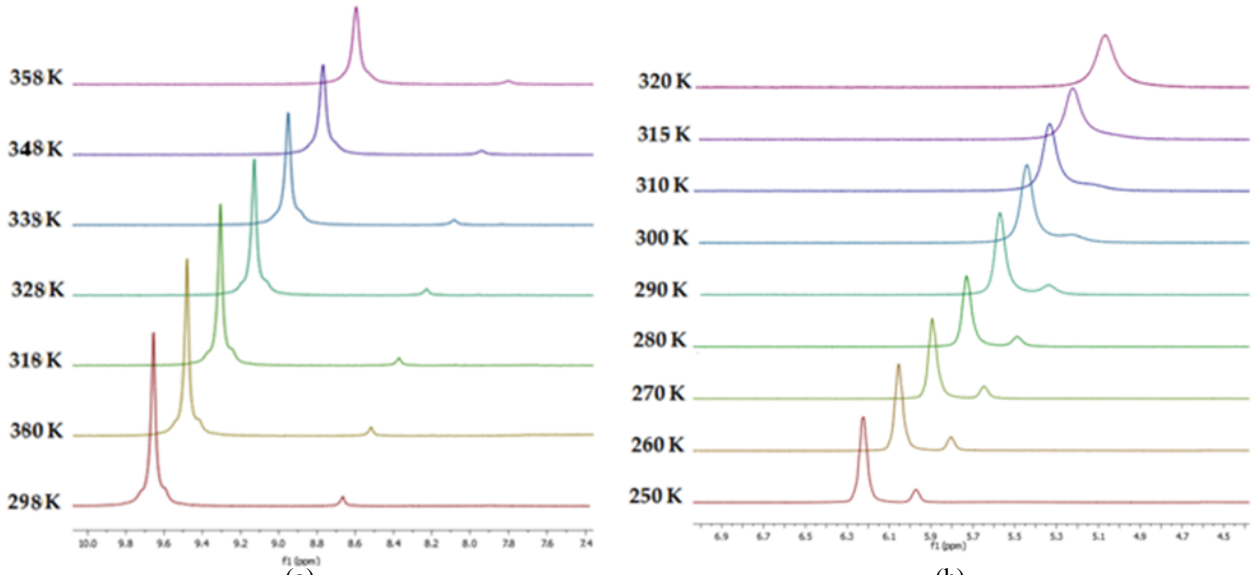


Figure 2: NH region of 1H NMR spectra of dicarbamates **2a** (a) and **2d** (b) in $CDCl_3$ + DMSO-d_6 at variable temperature.

Table II: Activation parameters measured for dicarbamates (**2c-f).**

Product	T_c(K)	$\Delta\upsilon_c$ (Hz)	Δp^a	$k_c(s^{-1})$	k_1 (s^{-1})	k_{-1} (s^{-1})	$\Delta G_1^{\#}$ ($kJmol^{-1}$)	$\Delta G_{-1}^{\#}$ ($kJmol^{-1}$)
2a	> 358	297.31	0.90	660.12	1254.23	66.01	>66.96	>75.11
2b	>340	441.36	0.95	979.95	1910.92	48.99	>62.28	>72.56
2c	300	62.55	0.93	138.88	247.20	30.55	59.73	67.79
2d	315	100.94	0.83	224.25	426.08	22.42	62.57	68.84
2e	310	63.75	0.65	141.54	233.54	49.54	61.57	67.21
2f	320	101.41	0.9	255.16	427.80	25.51	62.40	69.93

[a] $\Delta p = p_{s\text{-}cis} - p_{s\text{-}trans}$.

Table III: Activation parameters measured for dicarbamates (**3c-f**).

Product	T_c(K)	$\Delta\upsilon_c$ (Hz)	Δp^a	$k_c(s^{-1})$	k_1 (s^{-1})	k_{-1} (s^{-1})	$\Delta G_1^{\#}$ ($kJmol^{-1}$)	$\Delta G_{-1}^{\#}$ ($kJmol^{-1}$)
3a	>340	458.78	0.96	1018.63	1996.52	40.74	>62.15	>73.15
3b	>340	486.35	0.80	1079.85	1943.73	215.97	>63.89	>68.44
3c	318	6.0026	0.11	13.32	14.79	11.86	70.92	71.50
3d	350	128	0.32	284.20	375.14	193.25	68.93	70.86
3e	340	144.9	0.36	321.72	437.53	333.30	66.44	67.21
3f	330	138.1	0.34	306.62	410.87	202.37	64.58	66.52

[a] $\Delta p = p_{s\text{-}cis} - p_{s\text{-}trans}$.

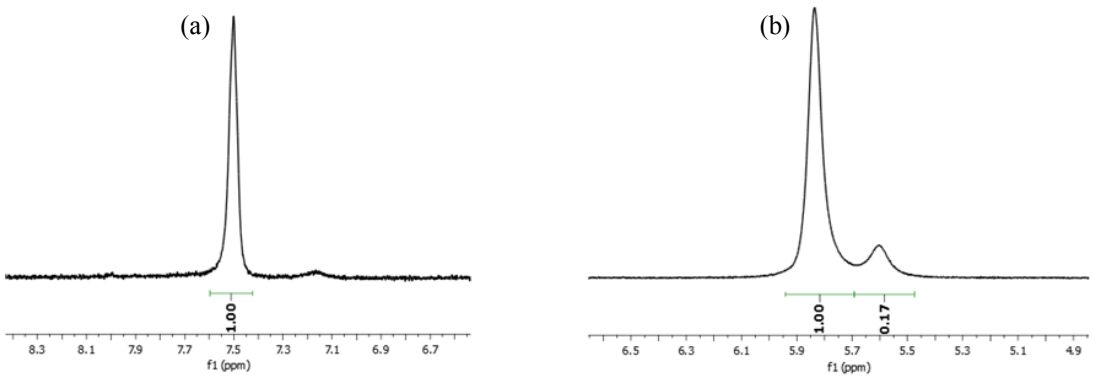


Figure 3: The NH region of ^{1}H NMR spectra of bis(thiocarbamate) **4d** (a) and its dicarbamate analogues **2d** (b) in CDCl3 + DMSO-*d*6 at room temperature.

by the fact that the electronic effects of the R group on the barrier to rotation in dicarbamates **2a-f** are more important than those due to steric hindrance in dicarbamates **3a-f** (Table III). However, the latter effect could not be excluded.

In order to get more insights into the effect of substitution of oxygen by a sulfur atom on the rotation barrier around the N–CO bond in dicarbamates **2d-f,** the free energies of activation and corresponding coalescence temperatures of dicarbamates **2d-f** were compared with bis (thiocarbamates) **4d-f** obtained from reaction of ethane-1,2-dithiol with propyl, butyl and 2-chloroethyl isocyanates, respectively [30]. The results are gathered in Table IV.

The results reveal that bis(thiocarbamates) have lower energies of activation than the corresponding dicarbamate counterparts. A straightforward difference can already be seen from their variable temperature ^{1}H NMR spectra which show also for compound **2d** two broad NH features at room temperature, whilst only one NH broad signal was observed for its bis(thiocarbamates) analog **4d** at this temperature (Fig. 3). This is consistent with the less electron withdrawing nature of the S-alkyl group which would lead to a less partial double bond character of the N–CO bond giving lower barrier to rotation for the bis(thiocarbamates) compared to corresponding dicarbamates [38].

Table IV: Activation Parameters Measured for dicarbamates (**2d-f)** and bis(thiocarbamates) (**4d-f)**.

Product	T_c (K)	$\Delta G_1^{\#}$ (kJmol^{-1})	$\Delta G_{-1}^{\#}$ (kJmol^{-1})
2d	315	62.57	68.84
4d	315	61.98	67.30
2e	310	61.57	69.72
4e	298	58.95	66.82
2f	320	62.40	69.72
4f	310	59.17	65.64

CONCLUSIONS

A series of dicarbamates **2** and **3** were synthesized from the reaction of propan-1,3- diol or triethylene glycol with aryl/alkyl isocyanates. These products were obtained in good to excellent yields and characterized by different spectroscopic techniques. The effects of the *N*-substituent on the *s-cis/s-trans* conformation was studied using VT NMR spectroscopy and showed that the rotation around N–CO bond is slower for electron withdrawing groups compared to donor substituents with a more remarkable effect for dicarbamates as compared to bis(thiocarbamates).

EXPERIMENTAL

All commercially available chemicals including starting isocyanates and diols were used without any purification. All solvents were dried, distilled, and stored over molecular sieves (4A°). Melting points were measured using an "Electrothermal 9100" apparatus and are uncorrected. 1H (300 MHz) and 13C (75.47 MHz) NMR spectra were recorded with a Bruker AC 300 spectrometer. The VT NMR spectra were recorded with a Bruker AC 400 apparatus. Probe temperatures (±0.5 K) were measured with a calibrated digital thermocouple. TMS was used as the internal standard for 1H and 13C NMR spectroscopy. Infrared spectra were obtained on a

YL2000 FT-IR spectrometer. HRMS (ESI) data were recorded on a high-resolution Micromass micrOTOF-Q II 10027 spectrometer.

1. General procedure for the preparation of dicarbamates (2a-f and 3a-f):

To a solution of isocyanate (20 mmol) in 10 mL of dry THF, was added the diol (10 mmol) under nitrogen atmosphere and at room temperature. The reaction mixture was stirred for 48 h to obtain a cloudy solution. Then, 30 mL of petroleum ether was added and the mixture was stirred for few hours to have a white precipitate, which was filtered to give white solids. These products were purified by recrystallization in (CCl_4) to give white powders. Compounds **2a**, **3a** and **3b** were prepared as previously described [31-34].

Propylene-1,3-bis(N-benzylcarbamate) (2b).

White solid; mp 127.1°C; IR ($CHCl_3$) (υ_{N-H}) 3332, ($\upsilon_{C=O}$)1684, (υ_{C-N}) 1265 cm^{-1}; ^1H NMR (DMSO+$CDCl_3$, 400 MHz) δ 1.88(m, 2H), 4.08(t, $^3J_{H-H}$ 6Hz, 4H), 4.215(d, $^3J_{H-H}$ = 6Hz, 4H), 6.65 (broad signal (NH, *s-trans*)), 6.89(broad signal (NH, *s-cis*)), 7.15-7.25(m, H_{arom}); ^{13}C NMR (DMSO+$CDCl_3$, 75 MHz) δ 28.44, 44.04, 60.91, 126.54, 126.85, 127.93, 139.07, 156.34; HRMS $(M+Na)^+$ calcd for $C_{19}H_{22}N_2NaO_4$, 365.1469 found 365.1458.

Propylene-1,3-bis(N-cyclohexylcarbamate) (2c).

White solid; mp 106.8°C; IR ($CHCl_3$) (υ_{N-H}) 3324, ($\upsilon_{C=O}$)1684, (υ_{C-N}) 1229 cm^{-1}; ^1H NMR (DMSO+$CDCl_3$, 300 MHz) δ 1.12-1.77(m, 20H), 1.83(m, 2H), 3.23(m, 2H), 3.99(t, $^3J_{H-H}$= 8Hz, 4H), 6.84(broad signal (NH)); ^{13}C NMR (DMSO+$CDCl_3$, 75 MHz) δ 24.60, 25.13, 28.65, 32.64, 49.37, 60.35, 155.25; HRMS $(M+Na)^+$ calcd for $C_{17}H_{30}N_2NaO_4$ 349.2093, found 349.2099.

Propylene-1,3-bis(N-propylcarbamate) (2d).

White solid; mp 73.7°C; IR ($CHCl_3$) (υ_{N-H}) 3285, ($\upsilon_{C=O}$)1682, (υ_{C-N}) 1250 cm^{-1}; ^1H NMR (DMSO+$CDCl_3$, 400 MHz) δ 0.82(t, $^3J_{H-H}$= 6Hz, 8H), 1.42(m, 4H), 1.44(m, 2H), 2.99(m, 4H), 4.03 (m, 4H), 5.6(broad signal (NH, *s-trans*)), 5.84 (broad signal (NH, *s-cis*)); ^{13}C NMR (DMSO+$CDCl_3$, 75 MHz) δ 11.23, 11.37, 22.9, 23.44, 28.8, 41.36, 42.32, 60.78, 156.50, 158.74; HRMS $(M+Na)^+$ calcd for $C_{11}H_{22}N_2NaO_4$ 269.1474, found 269.1474.

Propylene-1,3-bis(N-butylcarbamate) (2e).

White solid; mp 97.9°C; IR ($CHCl_3$) (υ_{N-H}) 3290, ($\upsilon_{C=O}$) 1682, (υ_{C-N}) 1261 cm^{-1}; ^1H NMR (DMSO+$CDCl_3$, 300 MHz) δ 0.88(t, $^3J_{H-H}$= 6Hz, 6H), 1.22-1.44(m, 8H), 1.84(m, 2H), 2.98(q, $^3J_{H-H}$= 6Hz, 4H), 4.01(t, $^3J_{H-H}$=6Hz, 4H), 6.6(broad signal, (NH, *s-trans*)), 6.87(broad signal, (NH, *s-cis*)); ^{13}C NMR (DMSO+CDC_{l3}, 75 MHz) δ 13.48, 19.36, 28.65, 31.5, 40.45, 60.39, 156.09; HRMS $(M+Na)^+$ calcd for $C_{13}H_{26}N_2NaO_4$ 297.1781, found 297.1785.

Propylene-1,3-bis(N-2-chloroethyl carbamate) (2f).

White solid; mp 87°C; IR ($CHCl_3$) (υ_{N-H}) 3316, ($\upsilon_{C=O}$)1687, (υ_{C-N}) 1257 cm^{-1}; ^1H NMR (DMSO+$CDCl_3$, 400 MHz) δ 1.85(m, 2H), 3.305 (m, 4H), 3.46(m, 4H), 4.03(m, 4H), 6.76(broad signal (NH, *s-trans*)), 7.04(broad signal (NH, *s-cis*)); ^{13}C NMR (DMSO+$CDCl_3$, 75 MHz) δ 28.45, 41.40, 43.08, 57.37, 58.12, 60.76, 156.13, 156.34; HRMS $(M+Na)^+$ calcd for $C_9H_{16}Cl_2N_2NaO_4$ 309.0385, found 309.0373.

3,6-Dioxaoctylene-1,8-bis (N-cyclohexylcarbamate) (3c).

White solid; mp 81.2°C; IR ($CHCl_3$) (υ_{N-H}) 3329, ($\upsilon_{C=O}$)1683, (υ_{C-N}) 1224 cm^{-1}; ^1H NMR (DMSO+$CDCl_3$, 300 MHz) δ 1.06-1.68(m, 20H), 3.28(s, 4H), 3.37-3.56(m, 10H), 4.01(t, $^3J_{H-H}$= 4.5Hz, 4H), 7.10(d, $^3J_{H-H}$= 6Hz (NH)); ^{13}C NMR (DMSO+$CDCl_3$, 75 MHz) δ 24.81, 25.22, 32.85, 49.60, 69.23, 70.03, 155.47; HRMS $(M+Na)^+$ calcd for $C_{20}H_{36}N_2NaO_6$ 423.2471, found 423.2467.

3,6-Dioxaoctylene-1,8-bis(N-propylcarbamate) (3d).

White solid; mp 95.9°C; IR ($CHCl_3$) (υ_{N-H}) 3322, ($\upsilon_{C=O}$)1684, (υ_{C-N}) 1254 cm^{-1}; ^1H NMR (DMSO+$CDCl_3$, 400 MHz) δ 0.89(t, $^3J_{H-H}$= 8Hz, 6H), 1.50(sextuplet, $^3J_{H-H}$= 8Hz, 4H), 3.05(m, 4H), 3.61(s, 4H), 3.65(t, $^3J_{H-H}$= 4Hz, 4H), 4.16(t, $^3J_{H-H}$= 4Hz, 4H), 5.78(broad signal (NH, *s-trans*)), 6.11(broad signal (NH, *s-cis*)); ^{13}C NMR (DMSO+$CDCl_3$, 75 MHz) δ 11.22, 22.82, 42.29, 63.08, 69.29, 72.60, 156.39; HRMS $(M+Na)^+$ calcd for $C_{14}H_{28}N_2NaO_4S_2$ 343.1845, found 343.1845.

3,6-Dioxaoctylene-1,8-bis(N-butylcarbamate) (3e).

White solid; mp 56.8°C; IR ($CHCl_3$) (υ_{N-H}) 3314, ($\upsilon_{C=O}$)1683, (υ_{C-N}) 1259 cm^{-1}; ^1H NMR (DMSO+$CDCl_3$, 400 MHz) δ 0.845(t, $^3J_{H-H}$= 6Hz, 6H), 1.255(sextuplet, $^3J_{H-H}$= 8Hz, 4H), 1.37 (quintet, $^3J_{H-H}$= 8Hz, 4H), 2.97(q, $^3J_{H-H}$= 8Hz, 4H), 3.52(s, 4H), 3.555(m, 4H), 4.05(t, $^3J_{H-H}$= 4Hz, 4H), 6.46(broad signal (NH, *s-trans*)), 6.84(broad signal (NH, *s-cis*)) ; ^{13}C NMR (DMSO $CDCl_3$, 75 MHz) δ 13.66, 19.57, 31.64, 40.08, 60.49, 62.99, 69.96 155.89, 156.26; HRMS $(M+Na)^+$ calcd for $C_{16}H_{32}N_2NaO_6$ 371.58, found 371.2145.

3,6-Dioxaoctylene-1,8-bis(N-2-chloroethylcarbamate) (3f).

White solid; mp 61.6°C; IR ($CHCl_3$) (υ_{N-H}) 3303, ($\upsilon_{C=O}$)1692, (υ_{C-N}) 1256 cm^{-1}; ^1H NMR (DMSO+CDC_{l3}, 400 MHz) δ 3.43(m, 4H), 3.51-3.59(m, 12H), 4.11(m, 4H), 6.62(broad signal (NH, *s-trans*)), 6.95(broad signal (NH, *s-cis*)); ^{13}C NMR (DMSO+CDC_{l3}, 75 MHz) δ 30.17, 35.29, 50.60, 67.18, 70.31, 162; HRMS $(M+Na)^{+}$ calcd for $C_{12}H_{22}Cl_2N_2Na_{O6}$ 383.0753, found 383.0746.

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