An Unsaturated Hydrogen Bonded Network Generated from Three-fold Symmetric Carbamates

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1. Materials and Methods

1.1. General

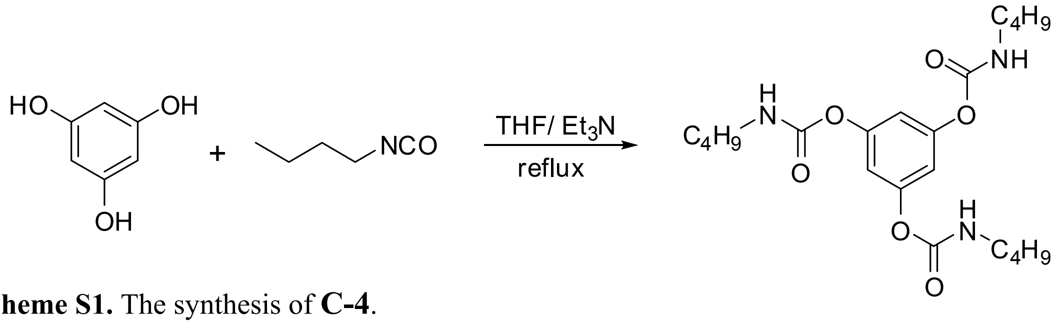
All the reagents were purchased from Alfa Aesar, Sigma-Aldrich, and used without further purification. Thin layer chromatography (TLC) was performed on a silica gel W/UV 200 µm pre-coated plates. Nuclear magnetic resonance spectra (NMR) were recorded with Brucker ADVANCE (^{1}H: 500 MHz, ^{13}C: 125 MHz). All spectra were obtained in deuterium Chloroform (Chloroform-*d*). For Chloroform-*d* solution, the chemical shifts were reported as parts per million (ppm). Coupling constants were reported in Hertz (Hz). Data for ^{1}H-NMR spectra were reported as follows: chemical shift (ppm: referenced to protium), brs = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, p = pentet, h = heptet, m = multiplet, coupling constant (Hz), and integration. Single crystal X-ray data were recorded on Brucker Kappa Apex II Duo X-Ray Diffractometer with Mo $K\alpha$ (λ = 0.71073 Å) or Cu $K\alpha$ (λ = 1.54178 Å). Melting points (m.p.) were measured on a MEL-TEMP device, which was calibrated by using hydroquinone as a standard. The melting points are averages of three measurements. Infrared spectroscopy (IR) was recorded on Thermo Scientific Nicolet iS5 FT-IR spectrometer.

1.2. Synthesis

1.2.1. Synthesis of benzene-1,3,5-triyl tris(propyl-carbamate), (**C-3)**

Synthesis of **C-3** was reported in a previous published paper (See reference 5).

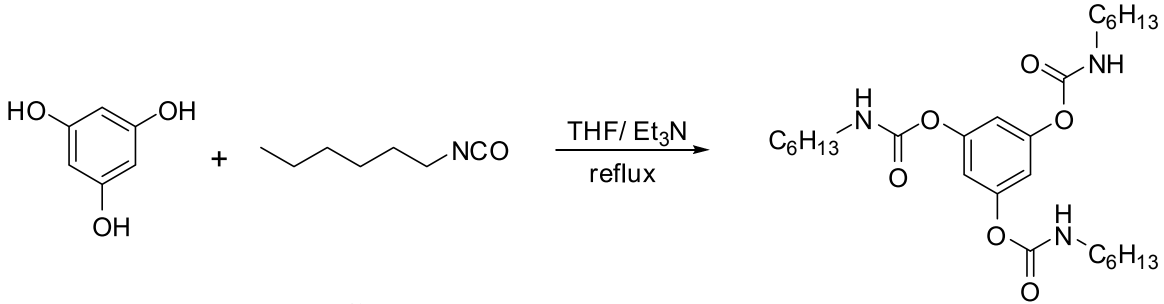
1.2.2. Synthesis of benzene-1,3,5-triyl tris(butyl-carbamate), (**C-4)**



Scheme S1. The synthesis of **C-4**.

A flame dried 50 mL round bottom flask equipped with a magnetic star bar was charged with 1-isocyanatobutane (0.72 g, 6 mmol) and a catalytic amount of triethylamine (4-6 drops) in 10 mL of THF. The mixture was stirred at room temperature for 5 minutes. Phloroglucinol (0.25 g, 2 mmol) in 5 mL of THF was added drop wise for 10 minutes. Then the mixture was refluxed for 16 hours. The mixture was concentrated by evaporating the solvent with a rotavapor and recrystallized in 25 mL of EtOAc. The title **C-4** (m.p. 130 – 132 °C) was obtained as a white solid (0.79 g, 93%). ^{1}H NMR($CDCl_3$, δ, ppm): 0.95 (t, J = 7.4 Hz, 9H), 1.38 (m, 6H), 1.54 (m, 6H), 3.24 (m, 6H), 5.04 (s, 3H), 6.85 (S, 3H); ^{13}C NMR ($CDCl_3$, δ, ppm): 14.1, 20.2, 32.2, 41.3, 112.2, 151.8. 154.1; IR (Nujol, υ, cm^{-1}) 3331, 3289, 2955, 2931, 1744, 1720, 1693, 1529, 1455, 1241, 1137.

1.2.3. Synthesis of benzene-1,3,5-triyl tris(hexyl-carbamate), (**C-6)**



Scheme S2. The synthesis of **C-6**.

A flame dried 100 mL round bottom flask equipped with a magnetic star bar was charged with 1-isocyanatohexanee (2.26 g, 18 mmol) and a catalytic amount of triethylamine (4-6 drops) in 10 mL of THF. The mixture was stirred at room temperature for 5 minutes. Phloroglucinol (0.75 g, 6 mmol) in 5 mL of THF was added drop wise for 10 minutes. Then the mixture was refluxed for 4 hours. The mixture was concentrated by evaporating the solvent with a rotavapor and precipitated in 250 mL of ice cold water. The solid product was filtered on a Buchner funnel and washed several times with deionized water. The title **C-6** (m.p. 130 – 131 °C) was obtained as a white solid (2.85 g, 93%). ^{1}H NMR($CDCl_3$, δ, ppm): 0.90 (t, J = 7.0 Hz, 9H), 1.28 – 1.44 (m, 18H), 1.65 (t, J = 7.1, 6H), 3.23 (m, 6H), 5.05 (s, 3H), 6.85 (s, 3H). ^{13}C NMR ($CDCl_3$, δ, ppm): 14.4, 23.0, 26.8, 30.2, 31.8, 41.6, 112.2, 151.8. 154.2. IR (Nujol, υ, cm^{-1}) 3332, 3290, 2954, 2927, 1745, 1719, 1693, 1533, 1458, 1240, 1142.

2. Spectra, data and images

2.1. Images of **C-4** and **C-6** Crystals

The crystals of **C-4** and **C-6** were obtained by slowly evaporating acetonitrile and acetonitrile/dichloromethane solution of the carbamates, respectively. Single crystal X-ray diffraction data of the compound was collected on a Bruker Apex Duo diffractometer with a Apex 2 CCD area detector at T = 100K. Cu radiation was used. All structures were process with Apex 2 v2013.4-1 software package with the most recent SAINT and SHELX software. Intrinsic phasing method was used to solve the structures after multi-scan absorption corrections (SADABS 2012/1). Details of data collection and refinement are given in the Table 1 and CIF files. INS and HKL files for **C-4** and **C-6** are inserted in the CIF. The crystallographic data for the three tri-cabamates are available in Cambridge Crystallographic Data Centre (CCDC# 987316 and 987317).

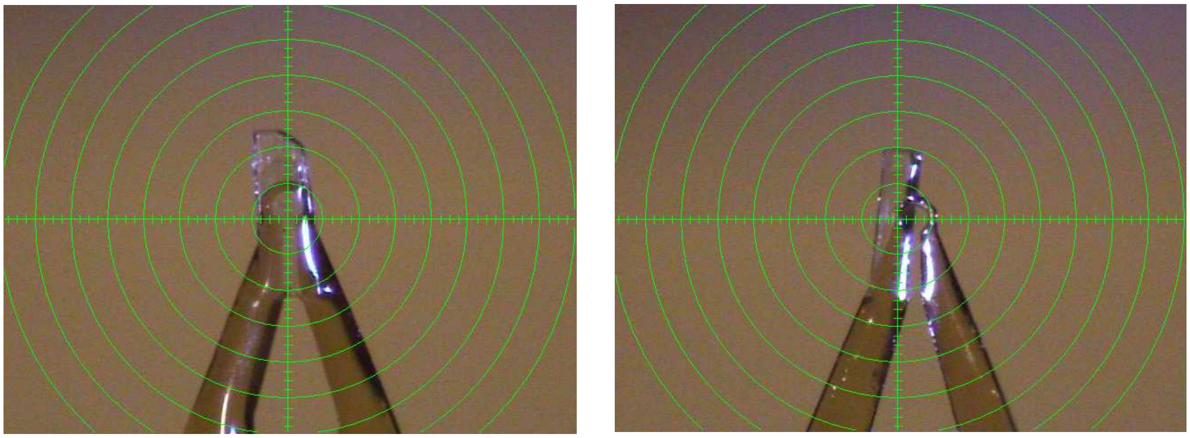
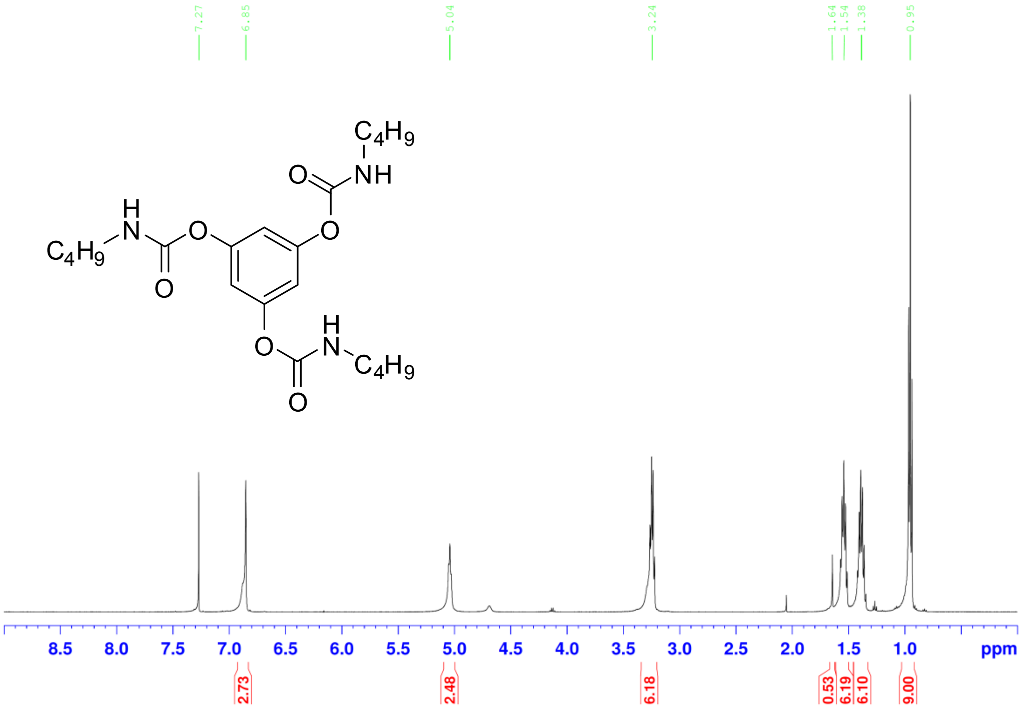


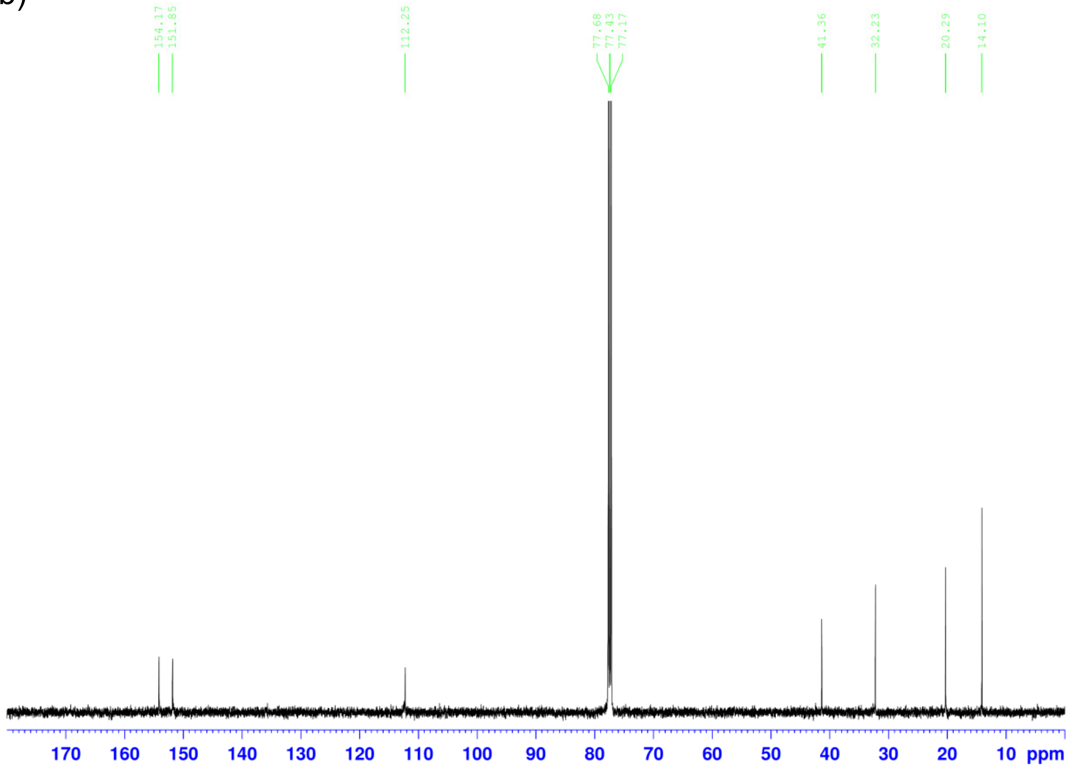
Figure S1. The images of single crystals of tri-carbamates **C-4** (left) and **C-6** (right).

2.2. ^1H , ^{13}C NMR and IR Spectra

(a)



(b)



(c)

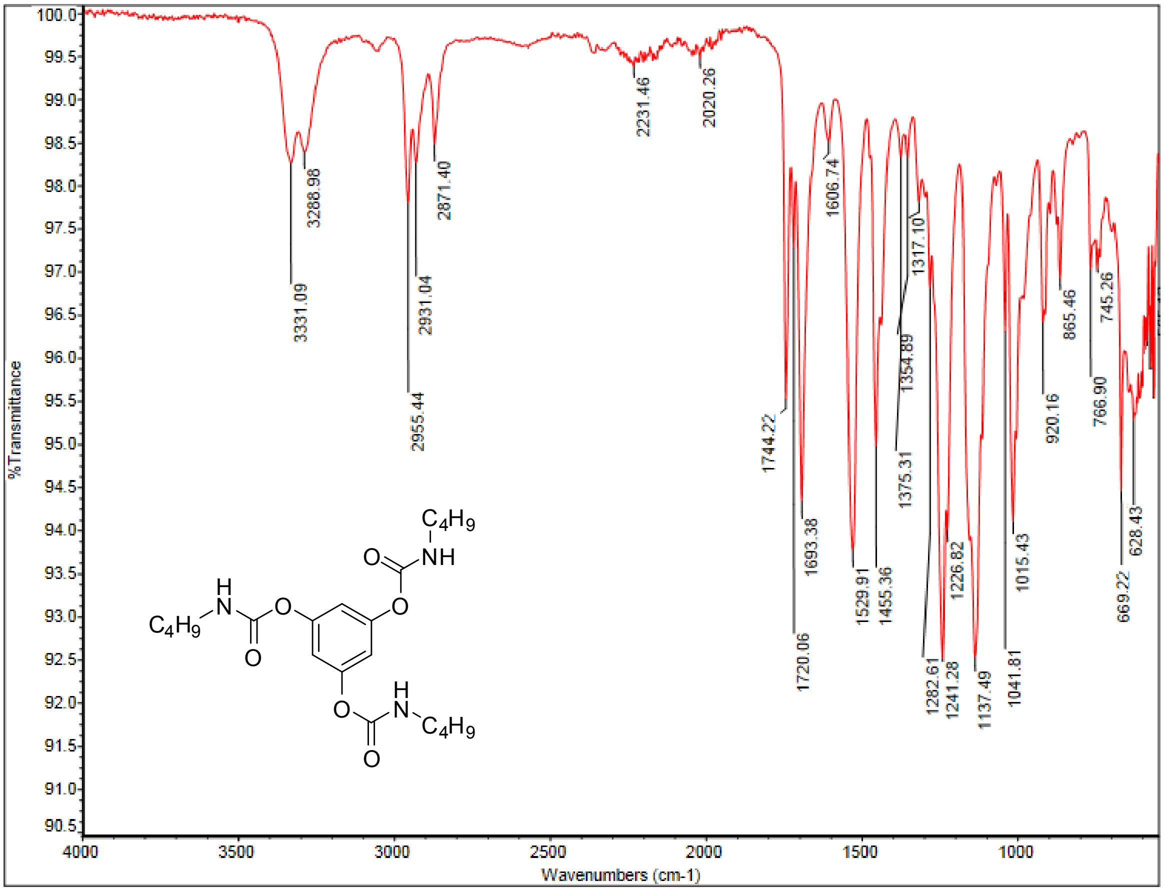
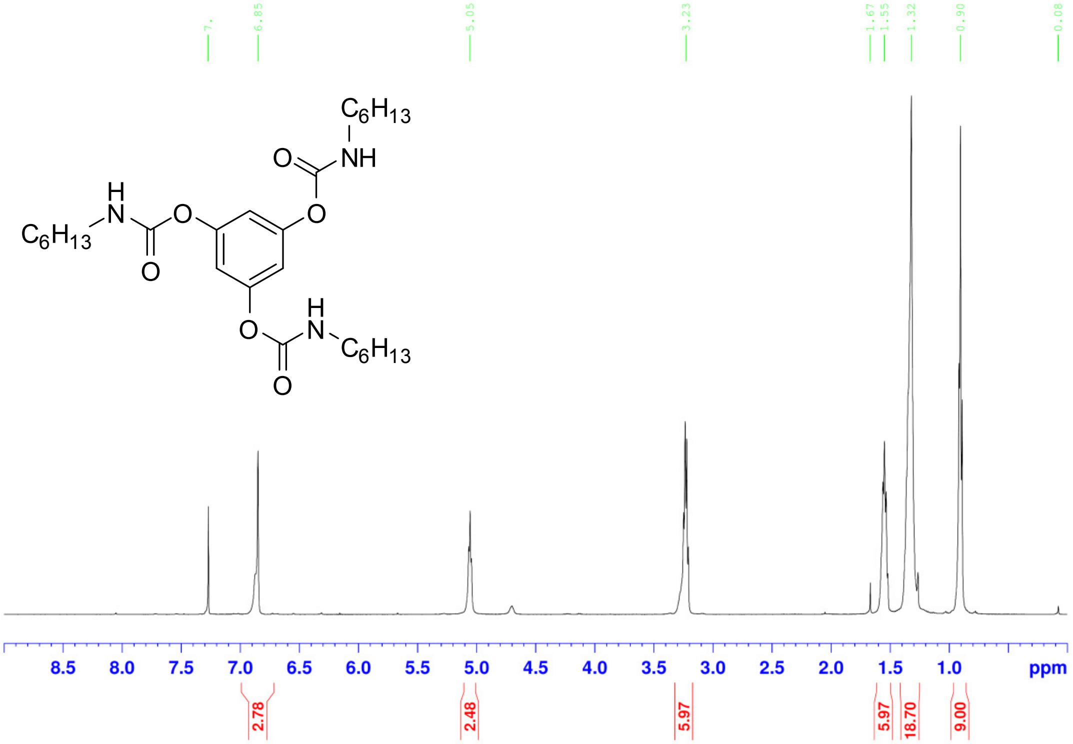
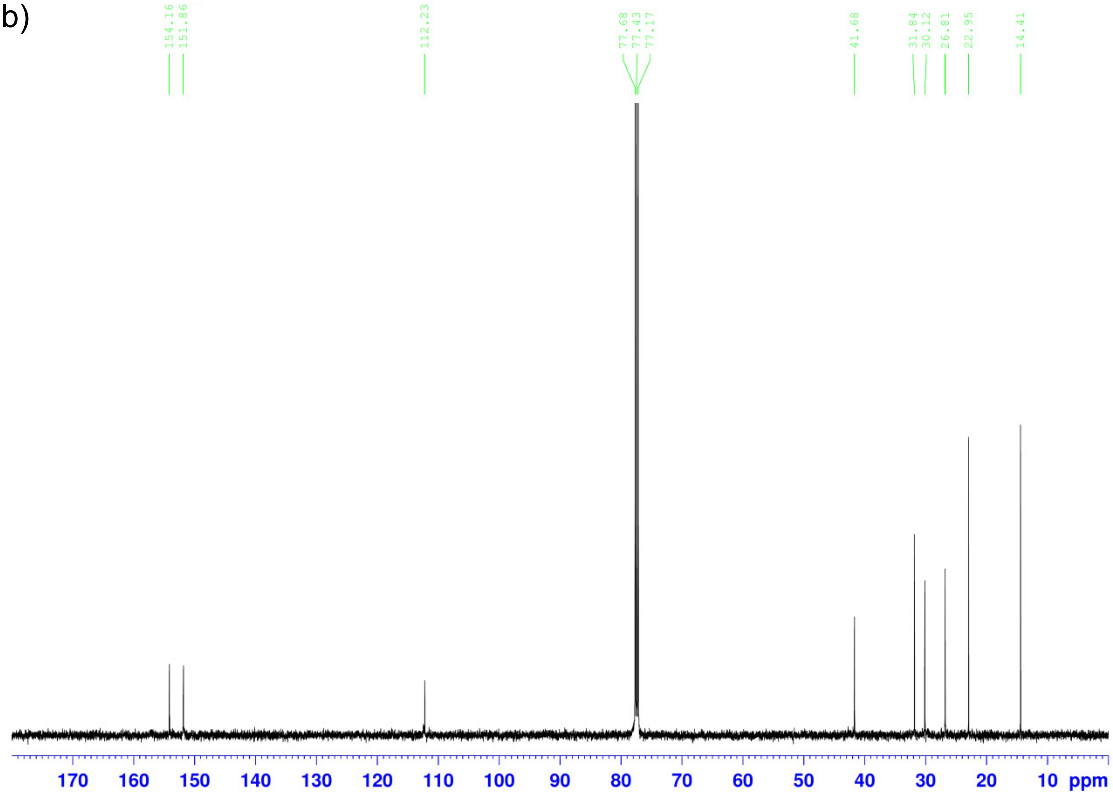


Figure S2. ^{1}H- (a) and ^{13}C- (b) NMR and IR (c) spectra of **C-4** at room temperature.

(a)


7.
6.85
5.05
3.23
1.67
1.55
1.32
0.90
0.08
C6H13
NH
O
O
H
N
C6H13
O
O
O
H
N
C6H13
O
O
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.78
2.48
5.97
5.97
18.70
9.00

(b)


154.16
151.86
112.23
77.68
77.43
77.17
41.68
31.84
30.12
26.81
22.95
14.41
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

(c)

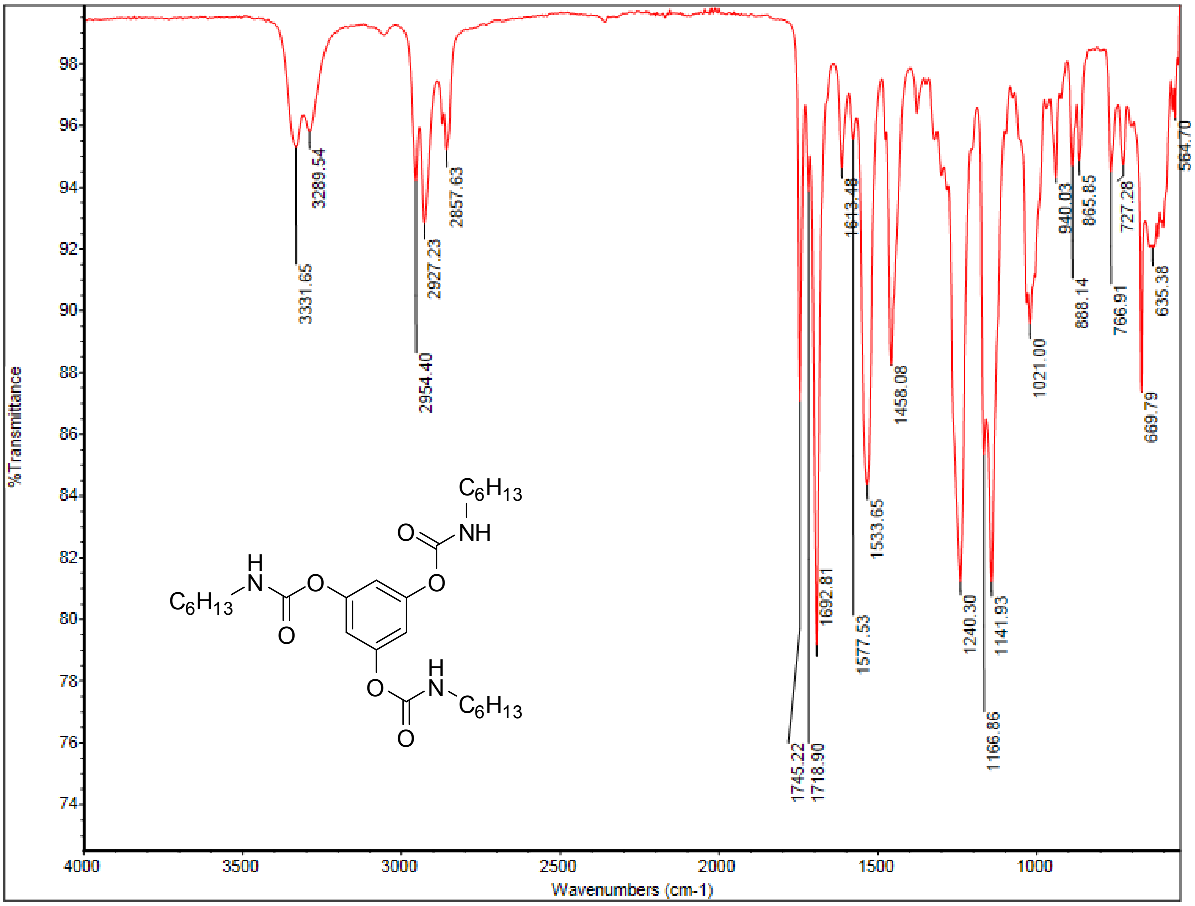


Figure S3. ^{1}H- (a) and ^{13}C- (b) NMR and IR(c) spectra of **C-6** at room temperature.

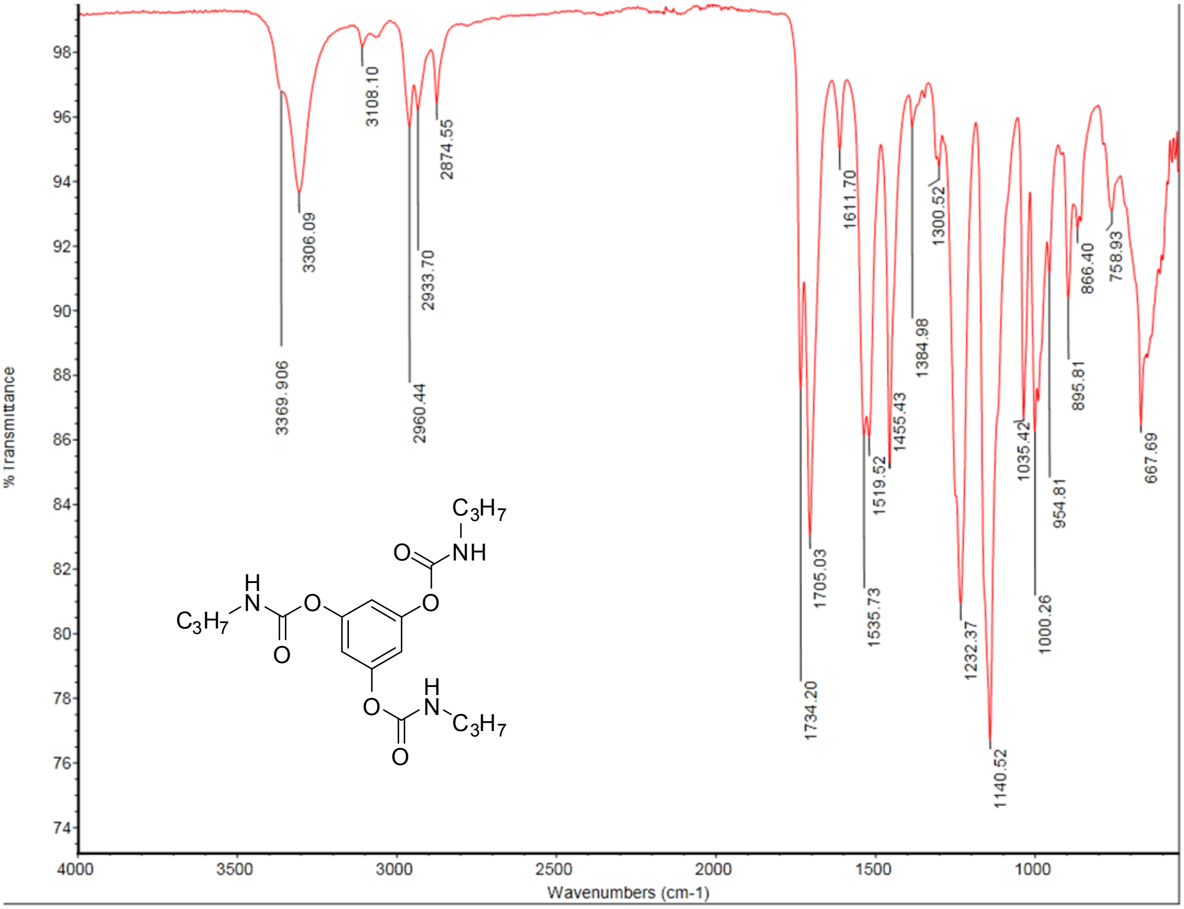


Figure S4. IR spectra of **C-3** at room temperature for comparison.

2.3. ^{1}H- NMR spectura of **C-6** in $CDCl_3$ at different concentration

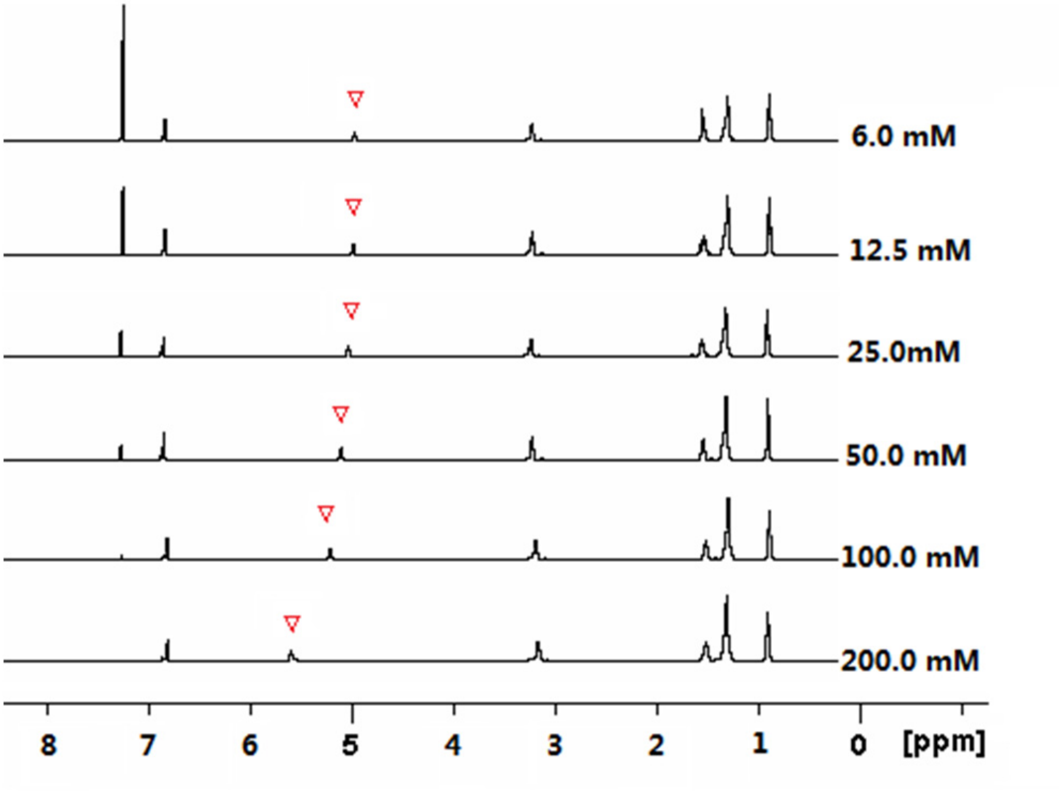


Figure S5. ^{1}H- NMR spectura of **C-6** in $CDCl_3$ at different concentration at room temperature.

2.4. ORTEP and Hydrogen Bond Table of **C-4** Crystal Structures

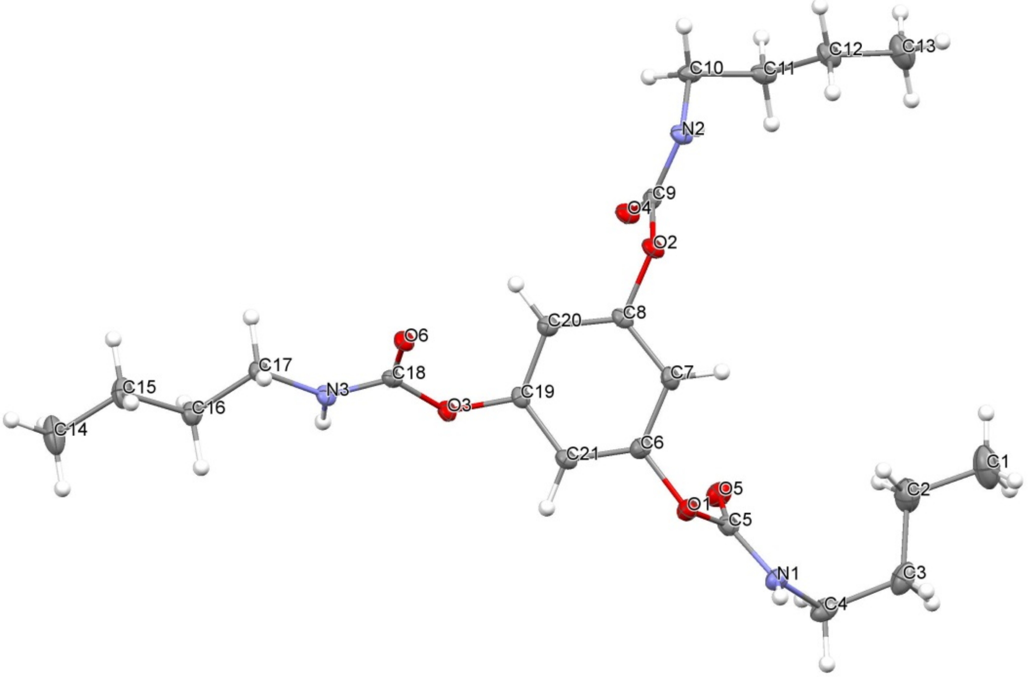


Figure S6. Oak Ridge thermal ellipsoid plot (ORTEP) representation of **C-4** at 30% electron density

Table S1: Hydrogen bonds of **C-4** with H...A < r(A) + 2.000 Å and <DHA > 110^{o}

D-H	**d(D-H)**	**d(H..A)**	**<DHA**	**d(D..A)**	**A**
N1-H1	0.880	2.022	175.08	2.9002(12)	O6 [-x, y-1/2, -z+1/2]
N2-H2	0.880	2.108	152.42	2.9170(11)	O6 [-x, -y+1, -z+1]
N3-H3	0.880	2.086	150.88	2.8869(12)	O4 [-x, -y+1, -z]
C10-H10A	0.990	2.627	165.28	3.5932(14)	O4 [x, -y+3/2, z+1/2]
C17-H17A	0.990	2.479	135.58	3.2606(14)	O5 [-x, -y+1, -z]

2.5. ORTEP and Hydrogen Bond Table of **C-6** Crystal Structures

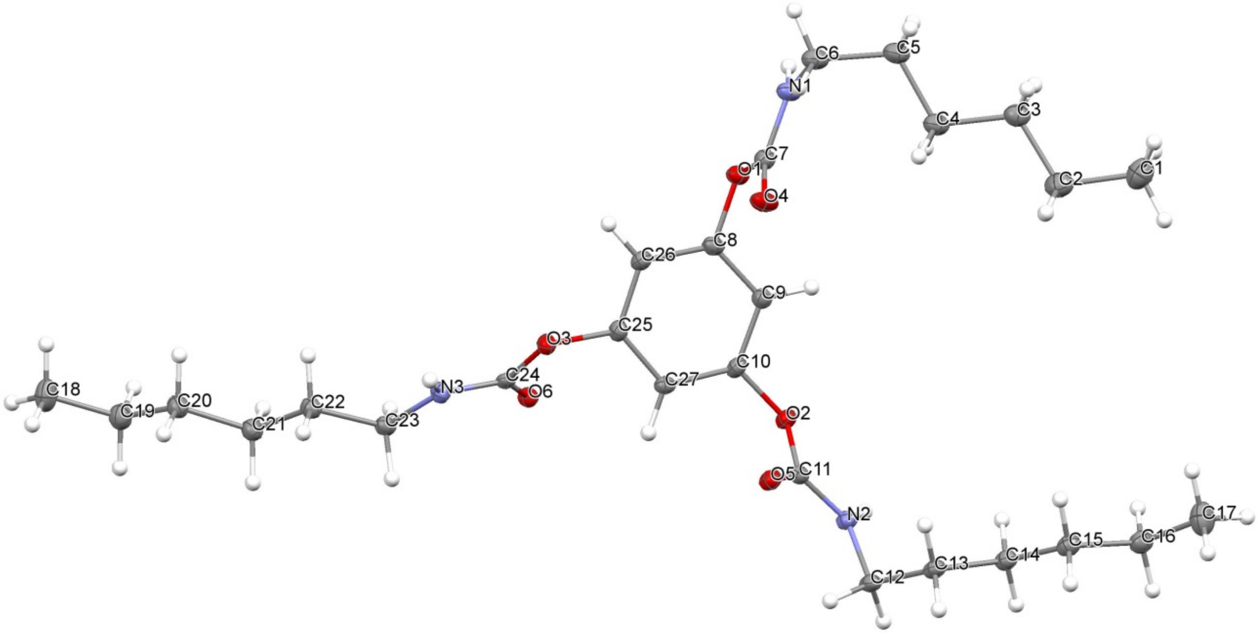


Figure S7. Oak Ridge thermal ellipsoid plot (ORTEP) representation of **C-6** at 30% electron density

Table S2. Hydrogen bonds of **C-6** with H...A < r(A) + 2.000 Å and <DHA > 110^{o}

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
N1-H1	0.880	2.023	178.83	2.9027(1)	O6 [-x, y+1/2, -z+3/2]
N2-H2	0.880	2.122	153.47	2.9354(2)	O6 [-x, -y+1, -z+1]
N3-H3	0.880	2.199	145.12	2.9640(2)	O5 [-x, -y+1, -z+2]
C23-H23A	0.990	2.444	138.30	3.2509(2)	O4 [-x, -y+1, -z+2]

2.6. Images of **C-6** Crystal Structure

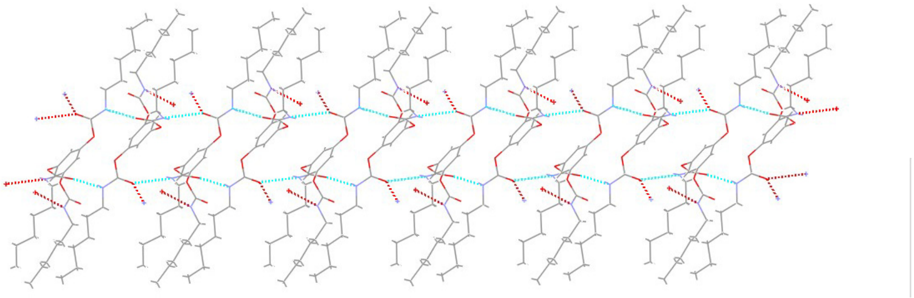


Figure S8. A side view of the hydrogen bonded ribbon of **C-6**

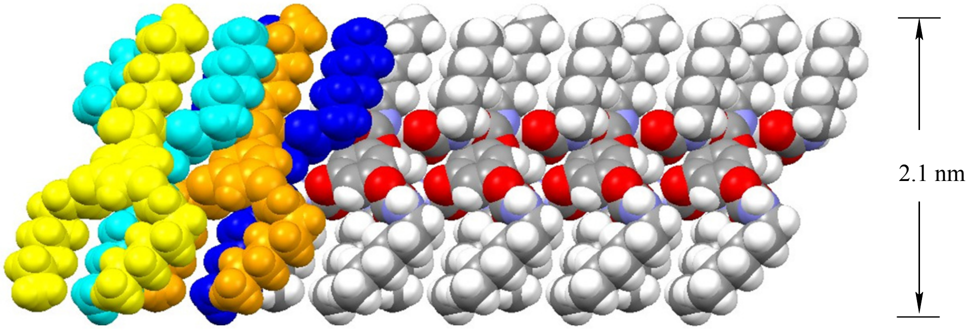


Figure S9. Hydrogen bonded ribbon of **C-6** in space-filling style

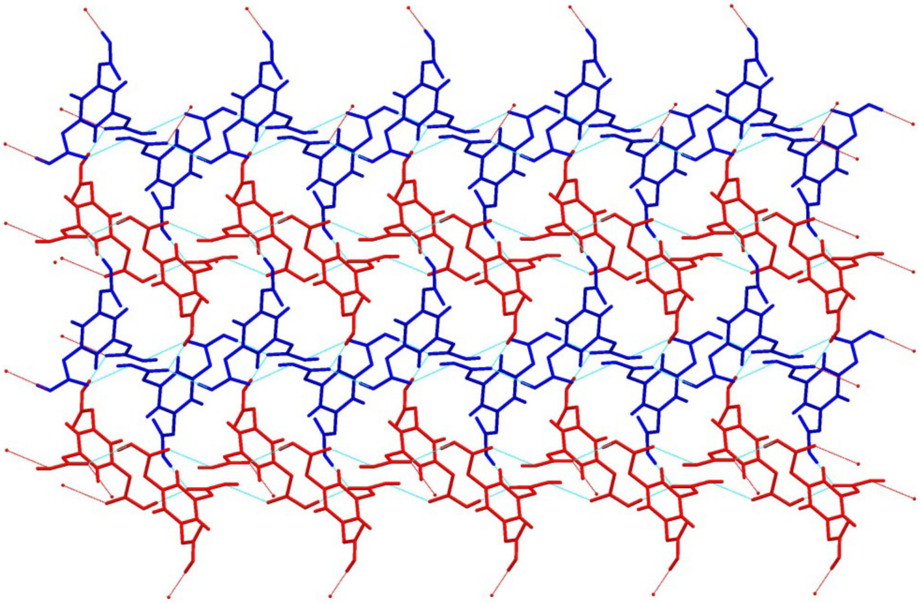


Figure S10. Hydrogen bonded sheet backbone of **C-6**. (hydrogen atoms are omitted and the side chains are replaced with carbon atoms for simplicity. Neighboring hydrogen bonded ribbons are shown in two colors for clarity.)

2.7. Packing of **C-4** and **C-6** sheets in Crystals

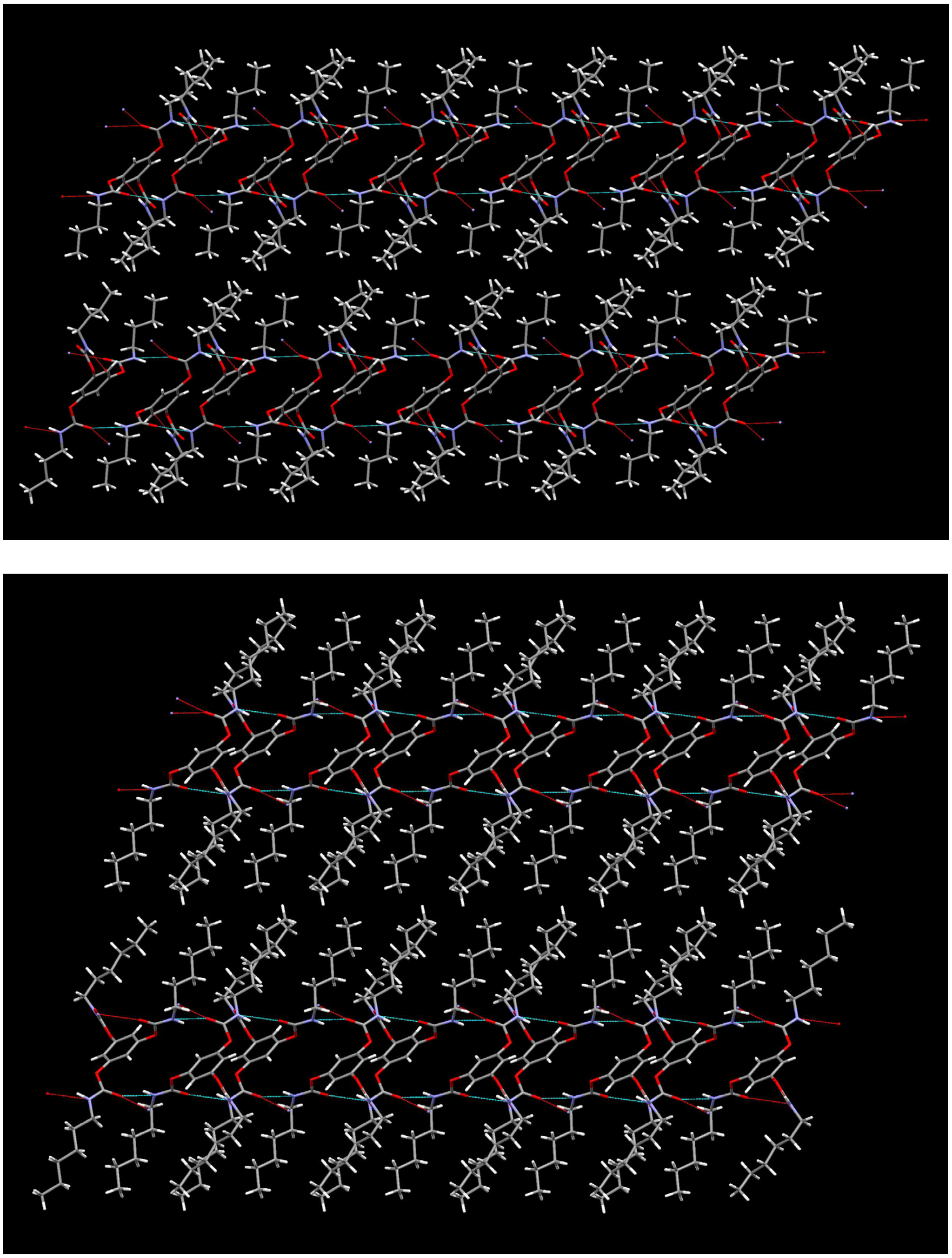


Figure S11. Crystal packing showing that there is no groove on the surfaces of the unsaturated sheet: a) side view of two layers of **C-4**; b) side view of two layers of **C-6**.