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(Citation)
Journal of Molecular Structure,752(1-3):93-97

(Issue Date)
2005-10

(Resource Type)
journal article

(Version)
Accepted Manuscript

(URL)
https://hdl.handle.net/20.500.14094/90000966

Three-Dimensional Supramolecular Assembly having Infinite Two-Dimensional Interlocking Networks built up only from Simple and Non-rigid Organic Molecules via Hydrogen Bonds. Crystal Structures of α,ω-diureidoalkanes $H_2N(CO)NH\text{-}(CH_2)_n\text{-}NH(CO)NH_2$ with $n = 4$ and 5

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Abstract

We determined the crystal structures of the title compounds $H_2N(CO)NH\text{-}(CH_2)_n\text{-}NH(CO)NH_2$ with $n = 4$ and 5 to check an idea that the replacement of the terminal methyl group of alkylurea $H_2N(CO)NH\text{-}(CH_2)_n\text{-}CH_3$ by a ureido group $\text{-}HN(CO)NH_2$ is useful to construct two and three-dimensional supramolecular assemblies with unique interlocking networks only from simple and non-rigid molecules via hydrogen bonds. The crystal structures of the two compounds were found to be quite similar to each other and the basic structure motif of each crystal was an infinite, two-dimensional network of the molecules connected via urea-chains formed by two NH···O hydrogen bonds (H-bonds) with graph-set $C_2^1(4)[R_2^1(6)]$. This network (single-network) comprised $(2n+18)$-membered open rectangular framework with graph-set $R_4^4(2n+18)$ composed of two molecules as a whole and two ureido groups. Two adjacent single-networks crossed each other to form a double-network characterized by catenane-type interlocks (i.e., an interpenetrating undulating two-dimensional (6,3) double-network). Neighboring double-networks related by center of symmetry were bridged by dimer-type H-bonds with graph-set $R_2^2(8)$ to give infinite, three-dimensional supramolecular assembly.

Keywords: catenane-type interlock, supramolecular assembly, diureidoalkane, crystal structure, crystal engineering

Introduction

For the design of molecular solids, the ureido group, $H_2N(CO)NH$-, is attractive owing to the coexistence of three hydrogen bond (H-bond) functionalities related to the supramolecular synthons shown in Scheme 1 [1-3]. Synthons 1 and 2 contribute to construct two distinct chain structures (urea-chains) and the third one, synthon 3, to combine molecules via dimer formation. The approximate orthogonality between synthons 2 and 3 seems favorable for the design of two-dimensional assemblies of molecules. In fact, cooperation of them plays important role in constructing a common two-dimensional plate-like supramolecular unit found for a series of alkylureas, $H_2N(CO)NH\text{-}(CH_2)_n\text{-}CH_3$ [4]. That is, urea-chains via synthon 2 are consolidated by synthon 3 to build the infinite two-dimensional unit. Interestingly, non-planar, twisted urea-chain is predominant in the crystals of the alkylureas with $n = 4\text{-}13$, planar one being found exceptionally for the crystal of alkylurea with $n = 3$. This twist of urea-chain leads to a crossed arrangement of alkyl groups and hence to unique two-dimensional molecular assemblies different from those expected from usual planar urea-chains.

In the crystals of alkylureas, the stacking of the supramolecular units is controlled by intermolecular hydrophobic interactions between the alkyl groups, and the contact between the terminal methyl groups is related by inversion center. This observation strongly suggests that exchange of the terminal methyl group of the alkylurea with a functional group having ability of intermolecular H-bond formation leads to three-, as well as two-, dimensional supramolecular structures. One may expect not only infinite two- or three-dimensional supramolecular assemblies, but also interlocking of the two-dimensional networks caused by the twist of the urea-chain (i.e., parallel interpenetration of undulating networks). Because crystal engineering of interpenetrating network structure has been a very attractive theme of supramolecular chemistry [5], we investigated the crystal structures of α,ω-diureidoalkanes, $H_2N(CO)NH\text{-}(CH_2)_n\text{-}NH(CO)NH_2$ with $n = 4$ and 5. Then the investigation indicated our prediction was valid, as will be shown in this paper.

Experimental

Material preparation: α,ω-Diureidoalkanes, C_4-du and C_5-du, were prepared from nitrourea and the corresponding primary diamines according to the literature for the synthesis of alkylureas [6]. Yields of C_4-du and C_5-du were 92 % and 91 %, respectively. Mp: 496 K (223 °C) for C_4-du and 507 K (234 °C) for C_5-du according to DSC measurements at a heating rate of 10 K/min. Single crystals of these compounds were crystallized from their aqueous solutions. The shape of the single crystals exhibited as a strange feature that they were looked just like fragments of broken glass. They lacked clear crystal faces, but were suitable for the single crystal X-ray works.

X-ray crystallography: A SMART 1000/CCD diffractometer was employed for the diffraction measurements of C_4-du and C_5-du at room temperature using graphite monochromated Mo-Kα radiations ($\lambda = 0.71073$ Å, $2\theta < 55$ °). The structure was solved by a direct method and refined by full-matrix least-squares calculations against F_o^2 with absorption corrections (SADABS) using a program package SHELXL-97 [7]. Non-hydrogen atoms were included in the structure refinements applying anisotropic displacement parameters. The positions of all hydrogen atoms were found in the difference Fourier maps and they were included in the refinement with isotropic displacement parameters.

Crystal data and details of the data collection and processing for C_4-du: $C_6H_{14}N_4O_2$, $M = 174.21$, monoclinic, space group $C2/c$ (no.15), $a = 13.092(3)$, $b = 7.247(2)$, $c = 9.288(2)$ Å, $\beta = 103.348(4)$ °, $U = 857.4(4)$ Å^3, $Z = 4$. $T = 297$ K. $D_c = 1.350$ g cm^{-3}. $F(000) = 376$. Crystal dimensions: 0.26×0.20×0.08 mm, μ(Mo-Kα) = 0.103 mm^{-1}, 2344 reflections measured (index range h -16 to 16, k -5 to 9, l -11 to11), 895 unique (R_{int} = 0.0290). The final $R_1(F) = 0.0448$ for 651 ($>2\sigma(I)$) and $wR_2(F^2) = 0.1168$ and GOF =

1.136 for all reflections, $w^{-1} = [\sigma^2(F_o^2) + (0.0431p)^2 + 0.4158p]$ where $p = (F_o^2 + 2F_c^2)/3$, 83 parameters. Max. shift/esd = 0.000, $\rho_{max} = 0.041$, $\rho_{min} = -0.213$ eÅ^{-3} on final difference map.

Crystal data and details of the data collection and processing for C_5-du: $C_7H_{16}N_4O_2$, $M = 188.24$, orthorhombic, space group *Pccn* (no.56), $a = 8.200(1)$, $b = 13.084(2)$, $c = 9.235(2)$ Å, $U = 990.8(3)$ Å^3, $Z = 4$. $T = 298$ K. $D_c = 1.262$ g cm^{-3}. $F(000) = 408$. Crystal dimensions: 0.40×0.25×0.12 mm, μ(Mo-Kα) = 0.094 mm^{-1}, 5028 reflections measured (index range h -10 to 10, k -16 to 16, l -11 to 7), 1057 unique ($R_{int} = 0.0322$). The final $R_1(F) = 0.0393$ for 825 ($>2\sigma(I)$) and wR_2 $(F^2) = 0.1163$ and GOF = 1.049 for all reflections, $w^{-1} = [\sigma^2(F_o^2) + (0.0616p)^2 + 0.1776p]$ where $p = (F_o^2 + 2F_c^2)/3$, 92 parameters. Max. shift/esd = 0.000, $\rho_{max} = 0.035$, $\rho_{min} = -0.126$ eÅ^{-3} on final difference map.

Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free from charge, by quoting the publication citation and deposition number: CCDC-258222 and CCDC-258223 for C_4-du and C_5-du, respectively.

Results and Discussion

Molecular structures: The molecular skeletons of C_4-du and C_5-du adopt planar, all-*trans* conformation in the crystals. The molecular symmetry of C_4-du is C_i, while that of C_5-du is C_2. In C_4-du and C_5-du, the direction of the two C=O bonds in a molecule is parallel and anti-parallel, respectively.

A search of the Cambridge Structural Database revealed that the molecular structure of $H_2N(CO)NH-(CH_2)_2-NH(CO)NH_2$ (C_2-du) as an inclusion molecule in a crystalline compound of tetra-*n*-butylammonium rhodizonate is the only one α,ω-diureidoalkane molecule characterized by X-ray single-crystal structure determination [8]. The molecular skeleton of C_2-du is not planar and thus differs completely from those of C_4-du and C_5-du.

Crystal structures: The crystal structure of C_5-du projected along the *c* axis onto the *ab* plane is shown in Fig. 1, in which one can see clearly the crossed arrangement of the alkyl groups. The H-bond system of C_5-du seen approximately along the *b* axis is illustrated in Fig. 2. The N1$\cdots$O1 H-bonds (HB_d, 2.963(2) Å) make centrosymmetric dimer-structures (urea-dimer) with graph set $R_2^2(8)$ (according to Etter notation [9], see the eight-membered ring A in Fig.2) at the both ends of a molecule to result in an infinite linear aggregation of the molecules. Other two H-bonds, N1$\cdots$O1 (HB_{C1}, 2.990(2)Å) and N2···O1 (HB_{C2}, 3.005(2) Å), connect adjacent urea moieties related by a *c*-glide symmetry (parallel to the *b* axis) to build a twisted urea-chain, which is topologically corresponds to graph-set $C_2^1(4)[R_2^1(6)]$ (see the ···O=C-N-H··· four-membered chain and the six-membered ring B in Fig.2).

The basic structural motif of the crystal of C_5-du is an infinite, two-dimensional network via H-bond ($C_2^1(4)[R_2^1(6)]$), a portion of which is depicted in Fig. 3 by using space-filling models of atoms. This network, which will be referred to as single-network, comprises 28-membered open rectangular framework with graph-set $R_4^4(28)$ formed by two molecules as a whole and two ureido groups (see the ring C in Fig.2). It should be noted that the single-network is not flat, but folded into pleats having a dihedral angle of ca. 54 ° and this geometry enables the interlocking described below.

Two adjacent single-networks related by a *c*-glide symmetry (parallel to the *a* axis) interlock to each other to result in a double-network having catenane-like interpenetrations (i.e., an interpenetrating undulating two-dimensional (6,3) double-network, according to Wells notation [10]) as shown in Fig. 4. And furthermore neighboring double networks related by center of symmetry are bridged by the dimmer-type H-bonds with graph set $R_2^2(8)$ to form an infinite, three-dimensional supramolecular assembly (see Fig. 1).

The H-bond network in the crystal of C_4-du is quite similar to that of C_5-du, the lengths of the HB_{C1}, HB_{C2}, HB_d and the twist angle being 2.898(2), 3.051(2), 2.942(2) Å and ca. 56 °, respectively. Consequently, the overall crystal structure of C_4-du is composed of the supramolecular assembly (having infinite two-dimensional catenane-type interlocking networks) similar to that of C_5-du, except for the fact that it consists of 26-membered frameworks with graph-set $R_4^4(26)$ and the two urea-chains at the both ends of a molecule are parallel and anti-parallel to each other in C_5 and C_4-du crystals, respectively.

The presence of various types of interpenetrating networks has been already revealed, as mentioned above. The present interpenetrating network is, however, the first one that is built up only with simple and non-rigid organic molecules to our best knowledge.

Conclusion

The overall geometry of the H-bond system and the crossed arrangement of the alkyl groups in the supramolecular assemblies of alkylureas were found to persist in the crystals of C_4-du and C_5-du. In these crystals, each of the two ureido groups in a molecule participated in the same type of H-bond system. As a result, three-dimensional supramolecular assembly consisting of the infinite two-dimensional catenane-type interlocking networks via hydrogen bonds was realized.

Acknowledgement

This work was supported in part by a Grant-in-Aid No. 15550119 from Japan Society for the Promotion of Science.

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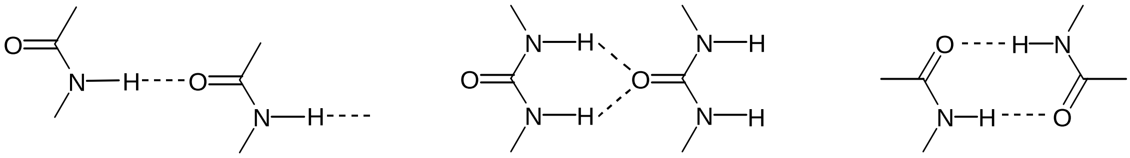


1 **2** **3**

Scheme 1

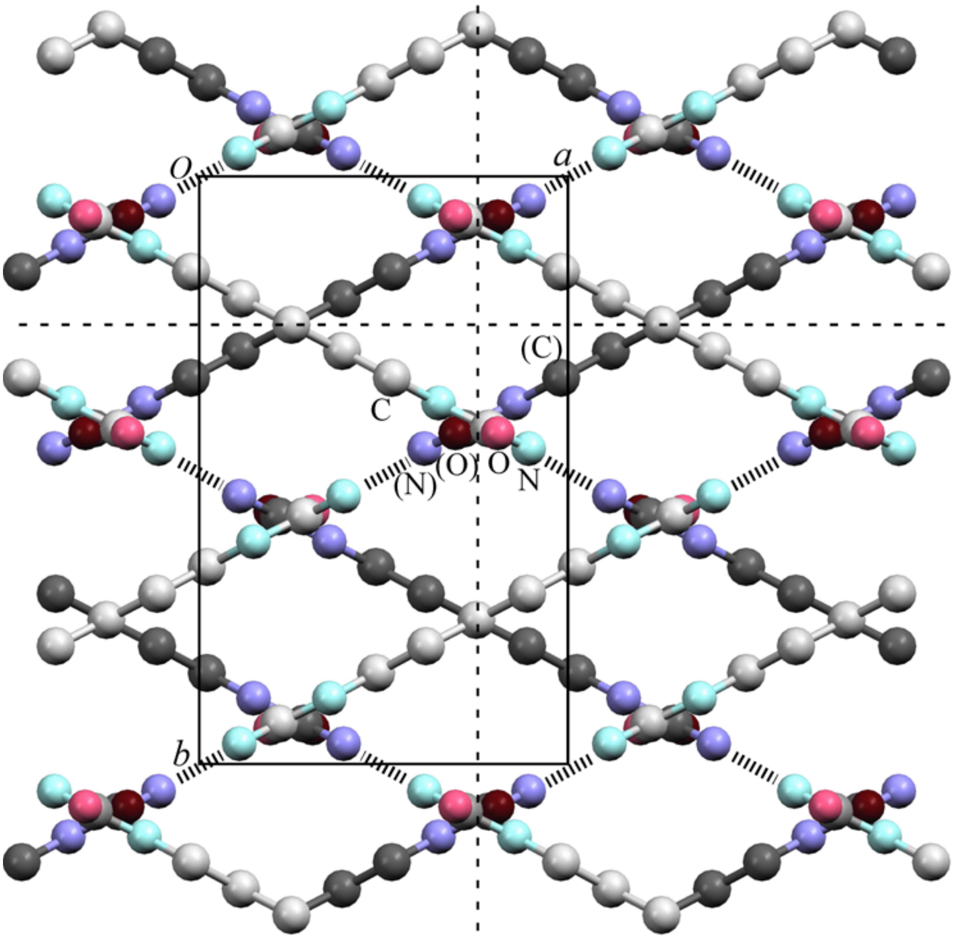
Figure captions

Fig. 1 Crystal structure of C_5-du viewed along the *c* axis of the space group *Pccn*. Hydrogen atoms are omitted for clarity. Molecules in the rear rank are darkened. Bold broken lines indicate dimmer-type H-bonds. Dotted lines indicate a part of the positions of *c*-glide planes.

Fig. 2 H-bond system in the crystal of C_5-du. HB_{C1}, HB_{C2} and HB_d indicate H-bonds with length of 2.990(2), 3.005(2) and 2.963(2) Å, respectively. The angle between the mean planes of adjacent ureido groups is 53.75(5) °. Symbols A, B and C correspond to graph-sets $R_2^2(8)$, $R_2^1(6)$ and $R_4^4(28)$, respectively.

Fig. 3 A portion of the two dimensional single-network of C_5-du illustrated by space-filling models of atoms. Hydrogen atoms are omitted for clarity. (a) and (b) are top and side views, respectively. The simplified net system and its terminology are shown in the right half of (a).

Fig. 4 Two dimensional double-network. (a) and (b) are top and side views, respectively. Hydrogen atoms are omitted for clarity. One single-network is whitened and the other darkened.



▮▮▮▮▮ : hydrogen bond

Fig. 1

Fig. 1 Crystal structure of C_5-du viewed along the *c* axis of the space group *Pccn*. Hydrogen atoms are omitted for clarity. Molecules in the rear rank are darkened. Bold broken lines indicate dimmer-type H-bonds. Dotted lines indicate a part of the positions of *c*-glide planes.

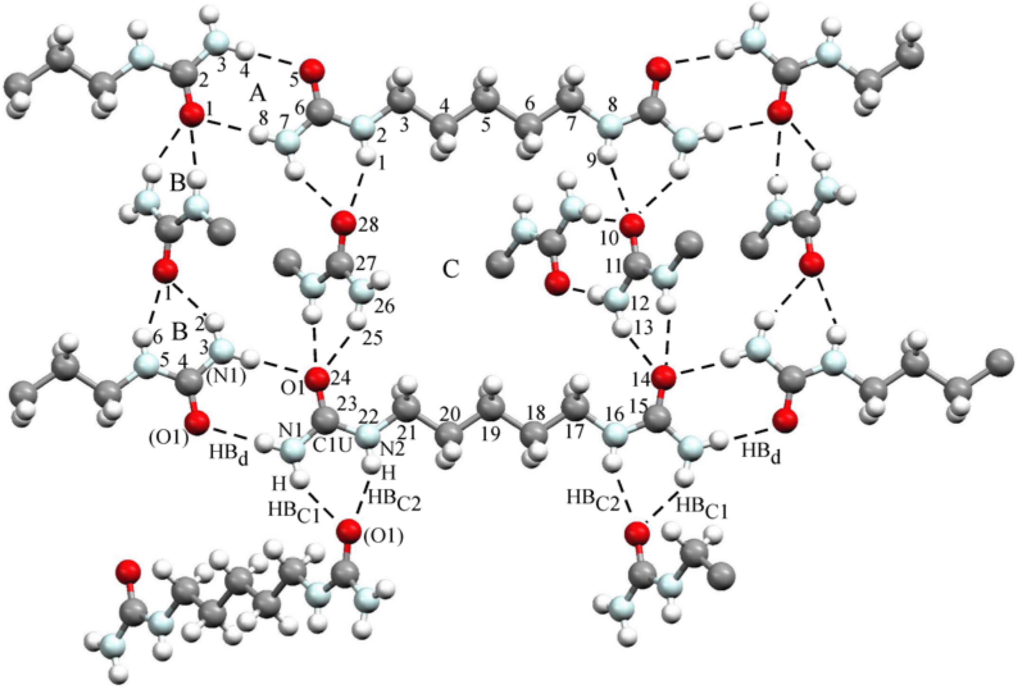
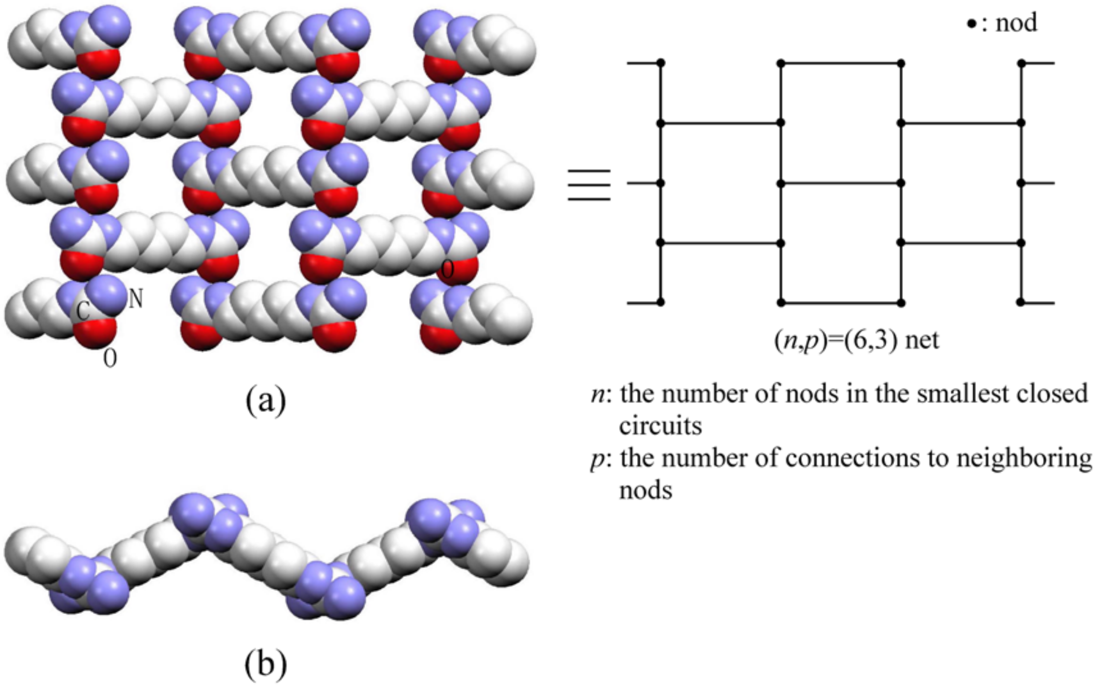


Fig. 2

H-bond system in the crystal of C$_5$-du. HB$_{C1}$, HB$_{C2}$ and HB$_d$ indicate H-bonds with length of 2.990(2), 3.005(2) and 2.963(2) Å, respectively. The angle between the mean planes of adjacent ureido groups is 53.75(5) °. Symbols A, B and C correspond to graph-sets $R_2^2(8)$, $R_2^1(6)$ and $R_4^4(28)$, respectively.



$(n,p)=(6,3)$ net

n: the number of nods in the smallest closed circuits

p: the number of connections to neighboring nods

Fig. 3

A portion of the two dimensional single-network of C_5-du illustrated by space-filling models of atoms. Hydrogen atoms are omitted for clarity. (a) and (b) are top and side views, respectively. The simplified net system and its terminology are shown in the right half of (a).

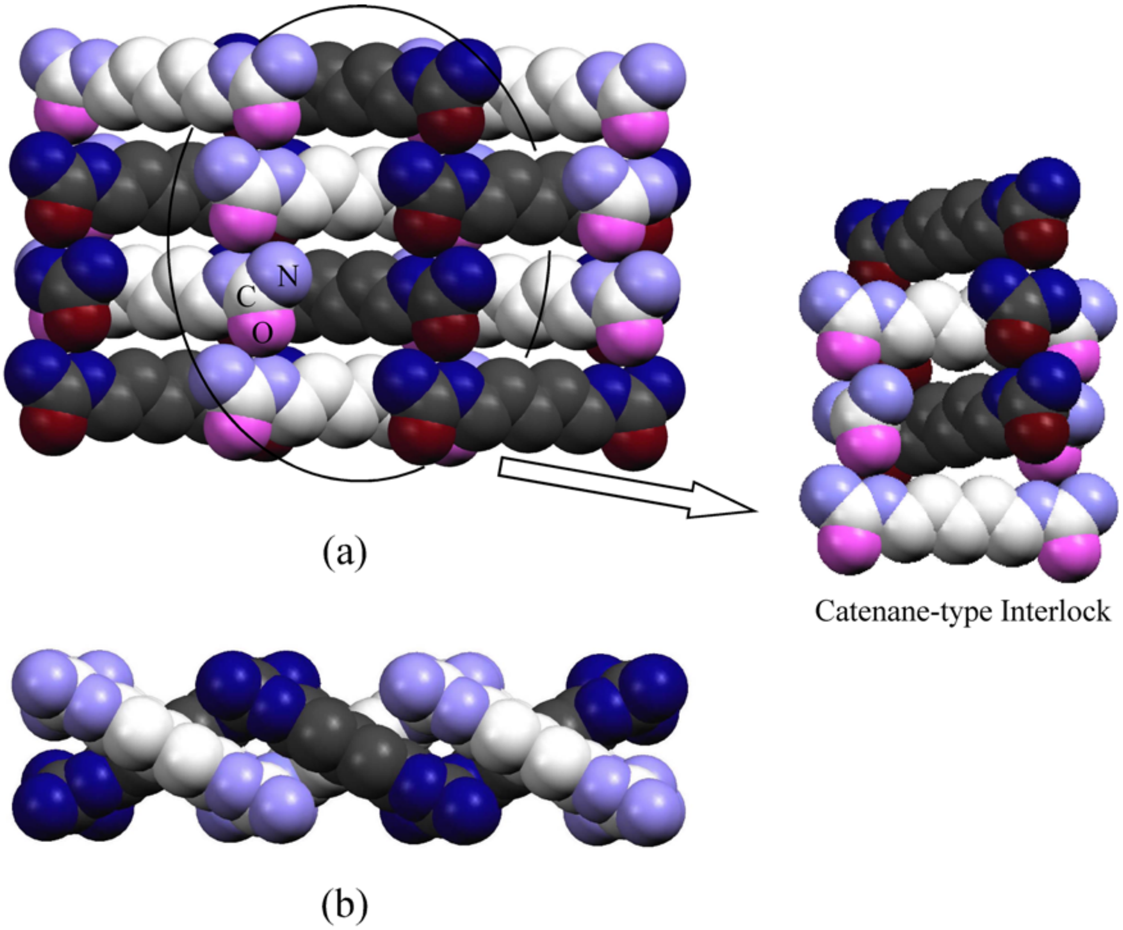


Fig. 4

Two dimensional double-network. (a) and (b) are top and side views, respectively. Hydrogen atoms are omitted for clarity. One single-network is whitened and the other darkened.