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TWO-DIMENSIONAL LATTICE OF SUPERBOATS COMPOSED OF SILICON-CENTERED TETRAHEDRA

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Four benzenecarboxylic acid groups attached to silicon, $(4\text{-}CO_2HC_6H_4)_4Si$, form an infinite two-dimensional pleated sheet in the solid state composed of cyclic units of 78 heavy atoms in the shape of a large boat-like structure held together by six complementary hydrogen-bonded units. Only three carboxylic acid groups per molecule are incorporated into the superboat. The material was crystallized from acetic acid. As a result, one molecule of acetic acid is bound to the fourth carboxylic acid group, preventing the structure from attaining a diamondoid lattice. Sixfold repetition of interpenetrating lattices restricts porosity. © 1997 by John Wiley & Sons, Ltd.

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INTRODUCTION

Self-assembly of infinite supramolecular networks[1] in the solid state initially emphasized one-dimensional structures, of which numerous examples of chains, rings, tapes, ribbons, strands or helixes have been constructed.[2] The fundamental or monomeric unit of such a structure requires two complementary binding units, such as carboxyl, amino or other groups. Construction of an infinite two-dimensional network requires three such complementary units to permit branching over a plane. The paradigm is trimesic acid (1,3,5-benzenetricarboxylic acid), which self-assembles in the crystal into an infinite planar sheet of interconnecting six-membered rings.[3] Subsequently, numerous lattice or sheet motifs have been described from crystal structures.[4] The planar nature of many of these arrays is determined by the planarity of the monomeric unit. There are fewer examples of non-planar, two-dimensional networks, which logically would be built out of non-planar rather than planar monomers.[4] In addition, there are several examples of truly three-dimensional networks or cages.[5] We report here a self-assembling, two-dimensional, non-planar network based on a silicon-centered tetrahedron.

RESULTS AND DISCUSSION

The subject of this study was tetrakis(4-carboxyphenyl)silane, $(4\text{-}CO_2HC_6H_4)_4Si$. 4-Bromotoluene was converted to its lithium derivative and allowed to react with tetrachlorosilane to give tetra(4-tolyl)silane.[6] Oxidation of the tolyl groups with potassium permanganate in pyridine and acidification with aqueous hydrogen chloride yielded the product.[7] Recrystallization from acetic acid produced crystals amenable to x-ray crystallography. Numerous other solvents were tried, but all failed to yield crystallographic-quality crystals.

The structure in the crystal is an infinite two-dimensional lattice formed by hydrogen bonding by three of the carboxyl groups to analogous carboxyl groups of neighbors. The fourth carboxyl group is capped by a molecule of solvent acetic acid, preventing the lattice from becoming truly three dimensional. Figure 1 illustrates the bonding arrangement of a single molecule and its four partners. Two of the carboxyl groups (type A) are paired with like partners from another monomer unit in traditional complementary carboxylic acid dimer structures. The dihedral angles between the paired carboxyl groups are 0° in both cases. For one of these carboxyl groups, the equivalence of the O—C bond distance (1.26 Å) indicates a symmetrical hydrogen bond, with the hydrogen atom equidistant from the partner oxygen atoms. For the other type A carboxyl group, there is a small difference between the O–C distances (1·24 and 1·28 Å). The O—C—O angle is 124° in both cases, and the plane of the carboxyl group is only slightly twisted from the attached benzene ring (OCCC dihedral angles of about 10°). The third carboxyl group (type B) is bonded symmetrically with solvent acetic acid (O—C distances of 1·24 and 1·26 Å, O—C—O angle of 124°, dihedral angle to the benzene ring of about 10°, angle between complementary

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carboxyl planes of about 13°).

The fourth carboxyl group (type C) engages in hydrogen bonding in an unusual fashion. The relatively unequal O—C distances (1·21 and 1·29 Å) indicate a less symmetrical hydrogen bond, and the O—C—O angle is opened to 133° (the dihedral angle to the benzene ring still is about 10°). A molecule of solvent acetic acid provides the remainder of a probable nine-membered hydrogen-bonded ring (not counting hydrogen atoms). This acetic acid is disordered, so that it was not fully refined and does not appear in the figure. Its disorder contributes to the *R* factor of 8·5%. Because it is shared between two monomeric units, it is represented as a half molecule. The interplanar angle between the benzoic acid carboxyl groups is 55° to permit inclusion of the acetic acid in the ring. The O—O distances between hydrogen-bonded pairs are 2·57 and 2·59 Å for the symmetrically bonded benzoic acids (type A), 2·60 and 2·62 Å for the benzoic acid bonded to acetic acid (type B) and 2·61 and 2·69 Å for the fourth carboxyl group (type C). The longer of the type C distances is to the half acetic oxygen and the shorter distance is between the two benzoic acid groups.

Figure 2 provides a view of a portion of the crystal lattice. The type A carboxyl groups form hydrogen-bonded pairs with like neighbors to create a one-dimensional ribbon. Each such ribbon is tied to analogous neighboring ribbons on either side by hydrogen bonding between type C carboxyl groups. Figure 2 shows several segments of two such ribbons and their type C connections. The type A and C hydrogen bonds form a repeating superboat unit composed of a ring of 78 heavy atoms (plus six presumed hydrogen atoms in the hydrogen bonds). The silicon atoms are at the corners of the superboat, whose sides, as measured by Si—Si distances, are 15·77, 15·95 and 16·15 Å. The type B hydrogen bonds (to acetic acid) protrude into the center of the superboat. Figure 3 illustrates diagrammatically the pleated sheet two-dimensional structure, in which the type B groups are omitted.

The superboat structure leaves sufficient space in the crystal for repetition of this structure in six interpenetrating lattices. The structure in Figure 2 or 3 has two parallel structures and three more running approximately perpendicular, all identical, leaving no channels. The structure thus allows for no enhanced porosity. The preference of a superboat over a superchair must result from interactions between groups in different planes and in different interpenetrating lattices.

EXPERIMENTAL

Tetra(4-tolyl)silane. A 100 ml round-bottomed flask was fitted with a Claisen adapter on which a condenser was

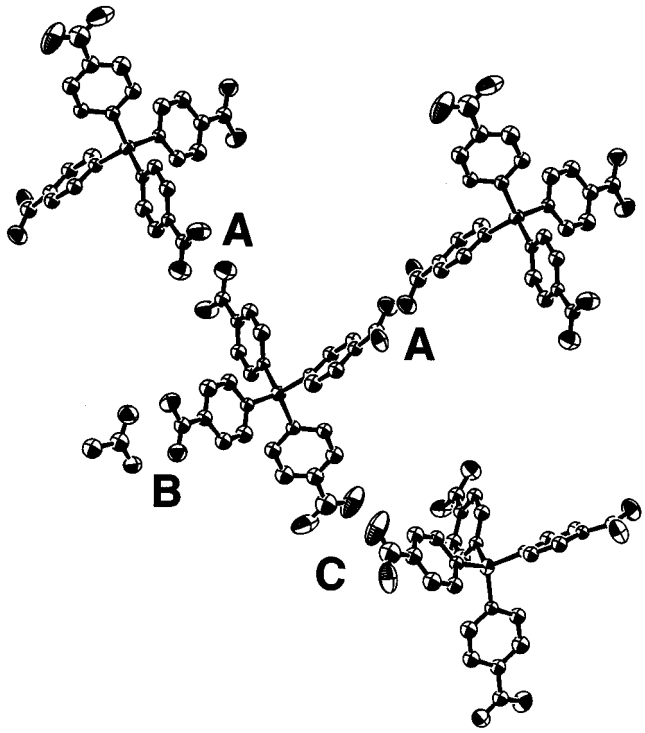

Figure 1. A single molecule of tetrakis(4-carboxyphenyl)silane with its four hydrogen bonding partners: three other identical molecules with two varieties of hydrogen bonds (A and C) and one molecule of acetic acid with a hydrogen bond labeled B

attached. The flask was charged with 0·88 g (127 mmol) of Li, 20 ml of anhydrous diethyl ether and a magnetic stirring bar. The system was flushed with N_2 and 10·34 ml (60·3 mmol) of 4-bromotoluene in 30 ml of anhydrous diethyl ether was added slowly with rapid stirring. An immediate exothermic reaction caused the ether to start boiling. The mixture was stirred for 30 min and 1·14 ml (10 mmol) of silicon tetrachloride was added dropwise. The mixture was stirred for an additional 30 min and quenched by the slow addition of 5 ml of water at 0 °C. Diethyl ether was removed by rotary evaporation and the product was isolated by vacuum filtration. Recrystallization from cyclo-

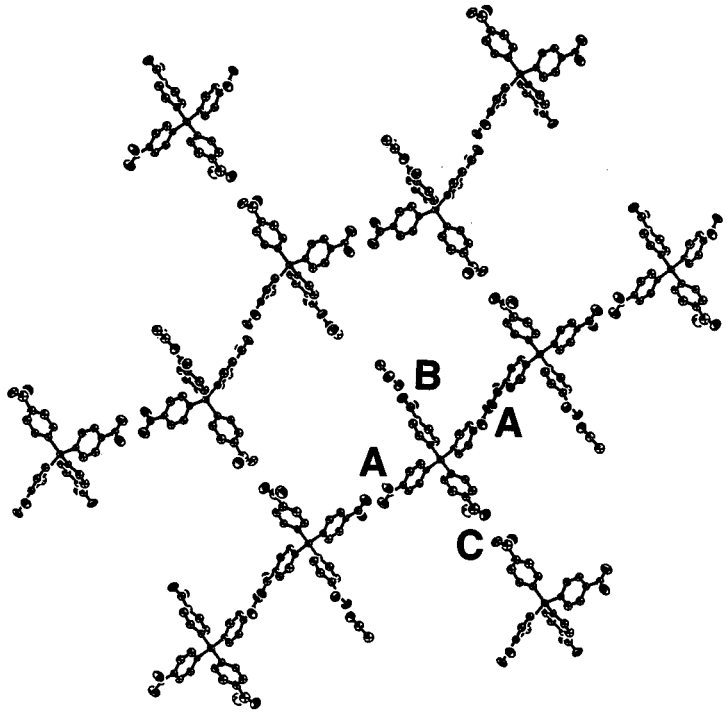

Figure 2. Portion of the three-dimensional lattice, showing the infinite chains formed by type A hydrogen bonds, the chain-linking type C hydrogen bonds and the non-linking type B hydrogen bonds to acetic acid. One complete superboat is illustrated

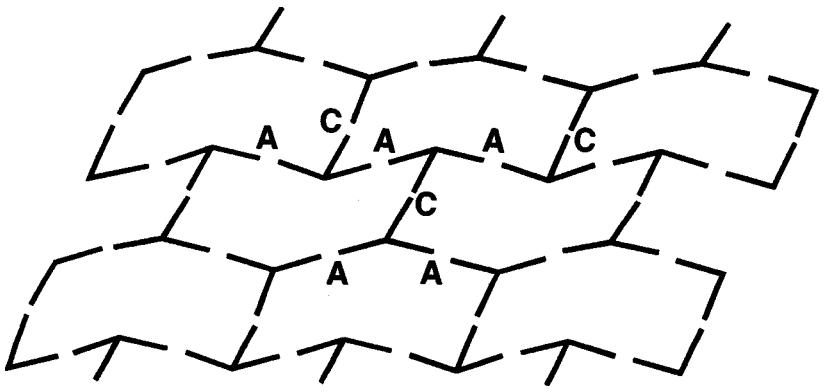

Figure 3. Diagram of eight superboats to illustrate the pleated sheet structure formed by the type A and C hydrogen bonds

hexane gave 3·59 g (92%) of a white solid: ^{1}H NMR ($CDCl_3$), δ 2·45 (s, 12H), 7·15 (d, 8H), 7·42 (d, 8H).

Tetrakis(4-carboxyphenyl)silane. A 100 ml round-bottomed flask was charged with 0·78 g (2 mmol) of tetra(4-tolyl)silane, 5·67 g (36 mmol) of $KMnO_4$, 10 ml of water and 30 ml of pyridine. The mixture was refluxed for 3 h. The flask was cooled to room temperature and 5 ml of CH_3OH was added slowly to decompose unreacted permanganate. Manganese dioxide was removed by vacuum filtration and the solid was washed with hot water. The filtrate was concentrated on a hot-plate to about 15 ml and concentrated HCl was added until the pH was 1. The resulting white solid was dissolved in dilute aqueous NaOH. The solution was filtered and reacidified with concentrated HCl. The new solid was collected and dried: 0·55 g (54%); ^{1}H NMR (acetone-d_6), δ 8·12 (d,8), 7·75 (d,8); ^{13}C NMR (acetone-d_6), δ 167·4, 139·1, 137·2, 133·0, 129·9; m.p. > 300 °C. For the tetramethylated ester derivative: ^{1}H NMR ($CDCl_3$), δ 8·03 (d,8), 7·59 (d,8), 3·90 (s,12); ^{13}C NMR ($CDCl_3$), δ 166·9, 138·1, 136·2, 131·7, 128·9, 52·3; found (calc.), C 67·82 (67·59), H 5·15 (4·96)%.

Crystal data for tetrakis(4-carboxyphenyl)silane. Colorless, transparent, prismatic crystal, $C_{28}H_{20}O_8Si{\cdot}1.5CH_3CO_2H$, 0·4 × 0·3 × 0·2 mm^3, M = 602·63, including 1·5 acetic acid molecules, primitive orthorhombic, space group *Pbcn* (≠60), a = 20·876(6), b = 18·255(2), c = 15·632(2) Å, U = 5957(1) Å^3, Z = 8, D_c = 1·34 g cm^{-3}, λ = 0·71069 Å, μ(Mo Kα) = 1·39 cm^{-1}, F(000) = 2512. Enraf-Nonius CAD4 diffractometer at −120 °C, direct methods (SHELXS86), 4612 unique absorption-corrected data, $2\theta_{max}$ = 45·9°, Si and O atoms refined anisotropically, C atoms refined isotropically, H atoms added in calculated position but not refined, one disordered acetic acid molecule present around the twofold axis. The final cycle of full matrix least-squares refinement was based on 1463 observed reflections with $I > 3{\cdot}00\sigma$ and 229 variable parameters and converged with R = 0·085 and R_W = 0·072. The maximum and minimum peaks in the final difference map were 1·42 and −0·45 e$^-$ Å^{-3}. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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