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Fivefold-Diamond Structure of Adamantane-1,3,5,7-tetracarboxylic Acid†

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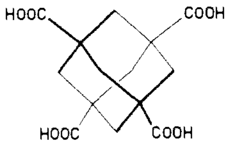
Abstract: An X-ray analysis shows adamantane-1,3,5,7-tetracarboxylic acid (**1**) to build up hollow hydrogen-bonded diamondlike ("diamondoid") lattices in the crystal. In order to fill their large empty cavities altogether five translationally equivalent diamondoid lattices mutually interpenetrate each other ("fivefold-diamond" structure). The diamondoid lattices are slightly tetragonally compressed with relatively long O(H)···O distances of 2.763 (1) Å for the hydrogen bonds. Implications of the present crystal structure analysis of **1** are pointed out regarding (i) the structure of tetrafunctional organic molecules with tetrahedrally directed substitutents in general, (ii) the prospective capability of diamondoid structures to act as hosts in host–guest inclusion compounds, and (iii) their use as models for the design of hypothetical "diamondoid polymers" potentially displaying isotropically extreme properties.

The four carboxylic groups of adamantane-1,3,5,7-tetracarboxylic acid (**1**) are directed tetrahedrally to a good degree of approximation. Given the task of predicting the crystal structure of **1** one would quite naturally suggest a diamondlike ("diamondoid") molecular arrangement (Figure 1): The adamantane cages of **1** play the role of the carbon atoms of diamond and are interconnected via pairs of hdyrogen bonds between the carboxylic groups as usually (yet not always) observed in crystalline carboxylic acids (Figure 2).[1] It should be noted that neither the tetrahedral orientation of the carboxylic groups in **1** nor the expected diamondoid crystal packing can be perfect, i.e., of cubic symmetry, since due to the substitution threefold symmetry axes are no longer possible in **1**. However, the respective deviations may be expected to be small considering the rigid carbon skeleton of **1**. The diamondlike lattice envisaged for crystalline **1** thus has the rather intriguing property of being composed of adamantane frameworks, which themselves may be thought of as cut out of another similar lattice of smaller dimensions, i.e., the diamond lattice itself. In other words, we are faced with a "super-diamond" structure (diamondoid lattice) made up of sections of the diamond lattice interconnected by hydrogen bonds between attached carboxylic groups.[2]



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The diamondoid crystal structure of **1** envisaged above has a serious disadvantage, which becomes clearly evident upon inspection of a model: The long distances *r* of about 10.0 Å between the centers of neighboring hydrogen-bonded molecules of **1** lead to very large empty spaces (Figure 5).[3] In order to avoid the related "horror vacui" dilemma, three possiblities may be considered: (1) severely distorted diamondoid lattices, possibly with patterns of hydrogen bonding different from the usual arrangement of Figure 2; (2) nondiamondoid packing modes; (3) several interpenetrating yet otherwise unconnected diamondoid lattices. In the case of the third, seemingly most sensible possibility, further conclusions may be drawn as outlined subsequently.[4]

On the basis of a single undistorted diamondoid lattice of **1** with $r = 10.0$ Å a density of only 0.336 g cm^{-3} may be estimated,[5] underscoring the hollowness of such a structure (Figure 5). The actual macroscopically measured density d_{measd} of **1** amounts to 1.65 g cm^{-3}, indicating no less than five interpenetrating hydrogen-bonded diamondoid lattices. For illustration, in Figure 3 the simpler case of two symmetrically interpenetrating diamond lattices ("double-diamond") is shown stereoscopically. Large macromolecular structures of this unique type have recently been inferred from X-ray diffraction data and electron microscopy for the double-diamondlike arrangement ($r = 91$ Å) of hydrogen-bonded water in a cubic lipid–water phase formed with glycerol monooleate[6a] and for certain so-called star block copolymers of styrene and isoprene, which consists of large polystyrene double-diamond networks ($r = 290$ Å) embedded in a polyisoprene matrix.[6b]

Our "fivefold-diamond" structure anticipated for crystalline **1** clearly represents a spectacular and unprecedented intermolecular architecture. We were thus keen to ascertain experimentally whether such an intriguing structure would really occur and performed an X-ray analysis of single crystals of **1**. Results and

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† Dedicated to Professor Jack Dunitz on the occasion of his 65th birthday.

(1) For packing modes of carboxylic acids, see: Leiserowitz, L. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1976**, *B32*, 775.

(2) A somewhat comparable structure of interest in the present context has recently been derived for Cd(SC$_6$H$_5$)$_2$: Craig, D.; Dance, I. G.; Garbutt, R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 165.

(3) As an inorganic analogue, the structure of the diamondlike cubic SiO$_2$ modification cristobalite (high-temperature form) may be cited. The openness of this structure, although much less pronounced than that of the hydrogen-bonded diamondoid lattice of **1**, is evident from the inclusion of cations in structures derived from cristobalite by replacing part of the silicon atoms by aluminum.

(4) Instead of a slightly distorted (cubic) diamondlike structure (zincblende, sphalerite) of **1** a slightly distorted hexagonal diamondlike structure (wurtzite) would be a reasonable alternative. However, according to model building the interpenetration possibilities of several wurtzite-type lattices appear more restricted than of diamond-type lattices. A very readable monograph on diamond has recently appeared: Davies, G. *Diamond*; Adam Hilger: Bristol, U.K., 1984. For hexagonal diamond (lonsdaleite), see: (a) Frondel, C.; Marvin, U. B. *Nature (London)* **1967**, *214*, 587. (b) Hanneman, R. E.; Strong, H. M.; Bundy, F. P. *Science (Washington, D.C.)* **1967**, *155*, 995.

(5) Obviously, the density *d* (g cm^{-3}) is given by $d = 1.660ZM_rV^{-1}$ where *Z* is the number of formula units per unit cell, M_r the molecular weight, *V* the volume of the unit cell (Å^3). With the help of Figure 1 one easily obtains $V = (^{16}/_3)^{3/2}r^3 = 12.3168r^3$ for the diamond lattice. Thus, $d = 1.0782M_rr^{-3}$ for a diamond-type structure ($Z = 8$).

(6) (a) Longley, W.; McIntosh, T. J. *Nature (London)* **1983**, *303*, 612. (b) Thomas, E. L.; Alward, D. B.; Kinning, D. J.; Martin, D. C.; Handlin, D. L.; Fetters, L. J. *Macromolecules* **1986**, *19*, 2197. Note the interesting relationships with mathematical minimal surfaces discussed in these papers. It is noted further that the lattice type of the intermetallic Zintl phase NaTl corresponds to a mixed double-diamond structure with a diamond lattice formed by the thallium atoms and another symmetrically interpenetrating one (cf., Figure 3) of the same size made up of the sodium atoms. See: Landolt-Börnstein *Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik und Technik*; Springer: Berlin, West Germany, 1955; Vol. 1, Part 4, p 30. Other inorganic examples of double-diamondlike structures are provided by the silicate mineral neptunite, by Cu$_2$O (cuprite), Zn(CN)$_2$ and Cd(CN)$_2$, and by three high-pressure modifications of ice: Cannillo, E.; Mazzi, F.; Rossi, G. *Acta Crystallogr.* **1966**, *21*, 200. Kamb, B.; Davis, B. L. *Proc. Natl. Acad. Sci. U.S.A.* **1964**, *52*, 1433. Kamb, B. *Science (Washington, D.C.)* **1965**, *150*, 205. See also: Liebau, F. *Structural Chemistry of Silicates*; Springer: Berlin, West Germany, 1985; p 128.

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Table I. Refined Atomic Parameters of Adamantane-1,3,5,7-tetracarboxylic Acid (**1**). Fractional Coordinates (C, O, $\times 10^5$; H, $\times 10^4$), Anisotropic Temperature Factor Coefficients for C and O (Å^2, $\times 10^4$), and Isotropic Temperature Factors for H (Å^2, $\times 10^3$) (Estimated Standard Deviations in Parentheses[a])

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	100000	25000	4512 (6)	208 (5)	225 (5)	168 (6)	0	0	13 (4)
C(2)	94158 (12)	2023 (12)	12470 (4)	213 (4)	172 (3)	229 (4)	1 (3)	−26 (3)	−14 (3)
C(3)	85620 (11)	16435 (11)	8483 (4)	172 (3)	197 (4)	179 (4)	−19 (3)	−24 (3)	−1 (3)
C(4)	70782 (12)	8654 (12)	4627 (5)	202 (4)	221 (4)	251 (5)	−56 (4)	−37 (4)	19 (3)
O(1)	60213 (11)	−2352 (12)	7544 (4)	293 (4)	460 (5)	352 (5)	−24 (4)	−47 (4)	−160 (3)
O(2)	68532 (11)	12621 (12)	−613 (4)	408 (4)	496 (5)	304 (5)	36 (4)	−162 (4)	−123 (4)
H(1)	9460 (17)	3354 (17)	181 (6)	38 (4)					
H(21)	9922 (20)	−731 (17)	1002 (6)	36 (3)					
H(22)	8493 (18)	−385 (18)	1484 (6)	38 (4)					
H_{ox}	5160 (30)	−679 (24)	466 (7)	85 (6)					

[a] $f = f^0 \exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{23}klb^*c^* + \ldots)]$.

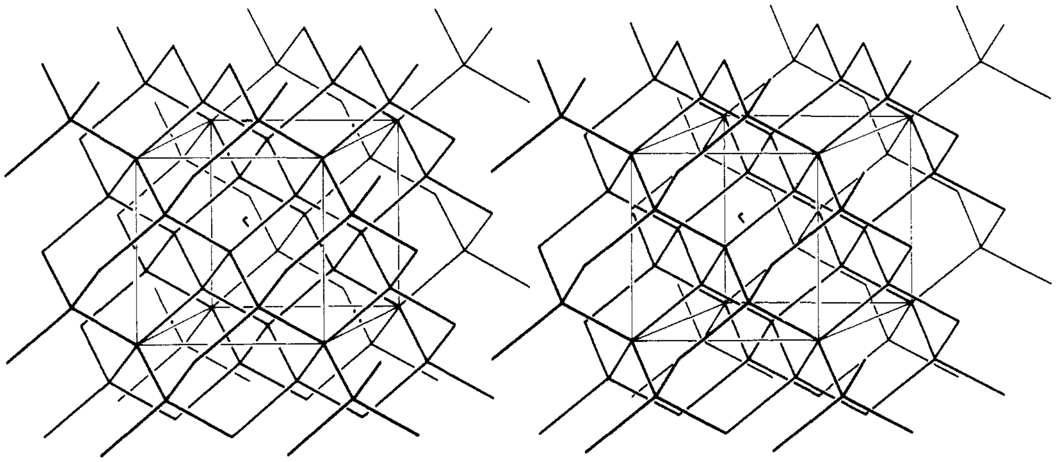


Figure 1. Stereoview of the diamond lattice with unit cell edges outlined.

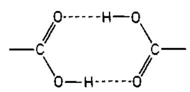
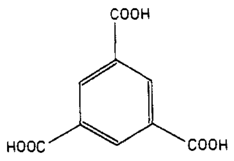


Figure 2. Commonly observed hydrogen bonding in carboxylic acids.

implications of this study are described in the following. It turned out that in the solid state **1** is indeed built up of five mutually interpenetrating super-diamond lattices, as visualized.

The crystal structure of **1** with its interpenetrating three-dimensional hydrogen-bonded diamondoid lattices may be viewed as a higher dimensional extension of the two-dimensional case of benzene-1,3,5-tricarboxylic acid (trimesic acid, **2**). The crystal structure of **2** was unravelled in the course of an outstanding X-ray study some 20 years ago[7] and consists of four interpenetrating sets of openly stacked, severely nonplanar (folded) hexagonal "chicken-wire" nets of trimesic acid molecules held together by pairs of hydrogen bonds (porous "super-graphite" sheets) much as in the present crystal structure of **1**. It was in fact the beautiful crystal structure of **2** that inspired us to think about how to add the third dimension to the system, having in mind as an analogy the formal structural transformation of graphite into diamond. (However, this analogy should not be carried too far since the stacking patterns of the folded hexagonal networks of **2** and the planar ones of graphite are different.) It is noted that the openness of a structure consisting of stacked super-graphite layers of **2** without mutual interpenetration is much smaller than that of a single hydrogen-bonded super-diamond lattice of **1**: A density of 0.93 g cm^{-3} may be estimated for planar noninterpenetrating chicken-wire sheets of **2** stacked 3.1 Å apart. The experimental density of **2** of 1.449 g cm^{-3} is larger by a factor of only 1.56 as compared with the analogous factor of 5 applying for **1**. The reason for this marked difference derives from the fact that the stacked hexagonal sheets of **2** have open channels only along one direction, i.e., normal to the sheets, and are otherwise compact, whereas the diamondoid lattice of **1** is hollow with respect to all three dimensions of space.



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The novel structural principle of interpenetrating diamondoid lattices outlined here is clearly generally relevant for tetrafunctional organic molecules with tetrahedrally directed substituents. Some further discussion of this point may be found in the concluding section of this report.

Experimental Section

Adamantane-1,3,5,7-tetracarboxylic acid (**1**)[8a,b] was prepared by alkaline hydrolysis of the corresponding tetraamide.[8c]

X-ray analysis: $C_{14}H_{16}O_8$; M_r 312.3; mp >390 °C (decomposition accompanied by gas evolution). Only very small crystals could be grown from solution by slow evaporation of the solvent, e.g., sparkling elongated octahedra from formic acid. Sufficiently large crystals of good quality were obtained as follows: The tetraacid **1**, which is water soluble only to a small extent, was dissolved as the tetracarboxylate in aqueous sodium hydroxide and the solution placed in a desiccator together with a beaker containing aqueous hydrochloric acid. After slow neutralization via the gas phase (about 4 days) up to 2-mm-long shiny tetragonal needles precipitated, which were about 0.2 mm thick and had well-developed faces at their tips.[9] A needle cut to a length of about 0.5 mm was used for the X-ray measurements: tetragonal space group $I4_1/a$ (No. 88), Z

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[7] Duchamp, D. J.; Marsh, R. E. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1969**, *B25*, 5.

[8] (a) Stetter, H.; Bänder, O.-E.; Neumann, W. *Chem. Ber.* **1956**, *89*, 1922. (b) Landa, S.; Kamycek, Z. *Collect. Czech. Chem. Commun.* **1959**, *24*, 4004. (c) We are indebted to H. Stetter, Aachen, for a sample of the tetraamide of **1**.

[9] This gas-phase neutralization procedure seems to be a rather effective technique for growing single crystals of water-insoluble weak acids, as we have observed in other similar cases.

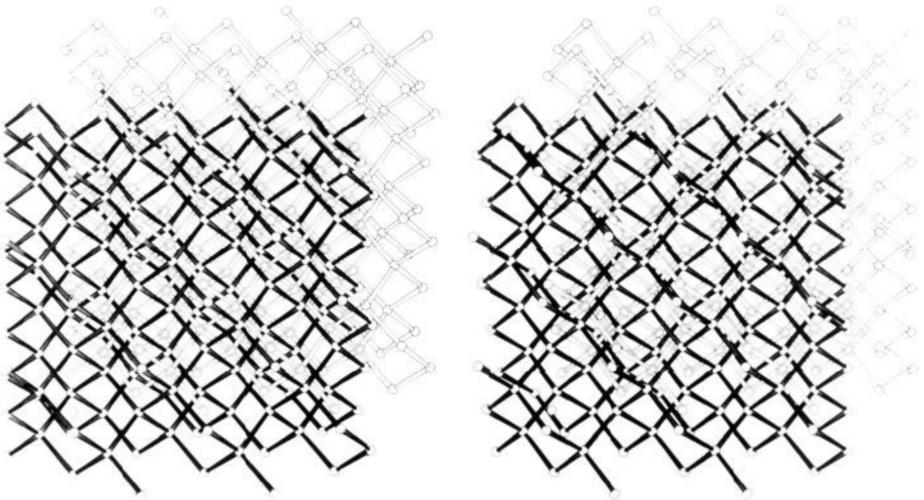

Figure 3. Stereoview of two symmetrically interpenetrating diamond lattices (double-diamond structure).

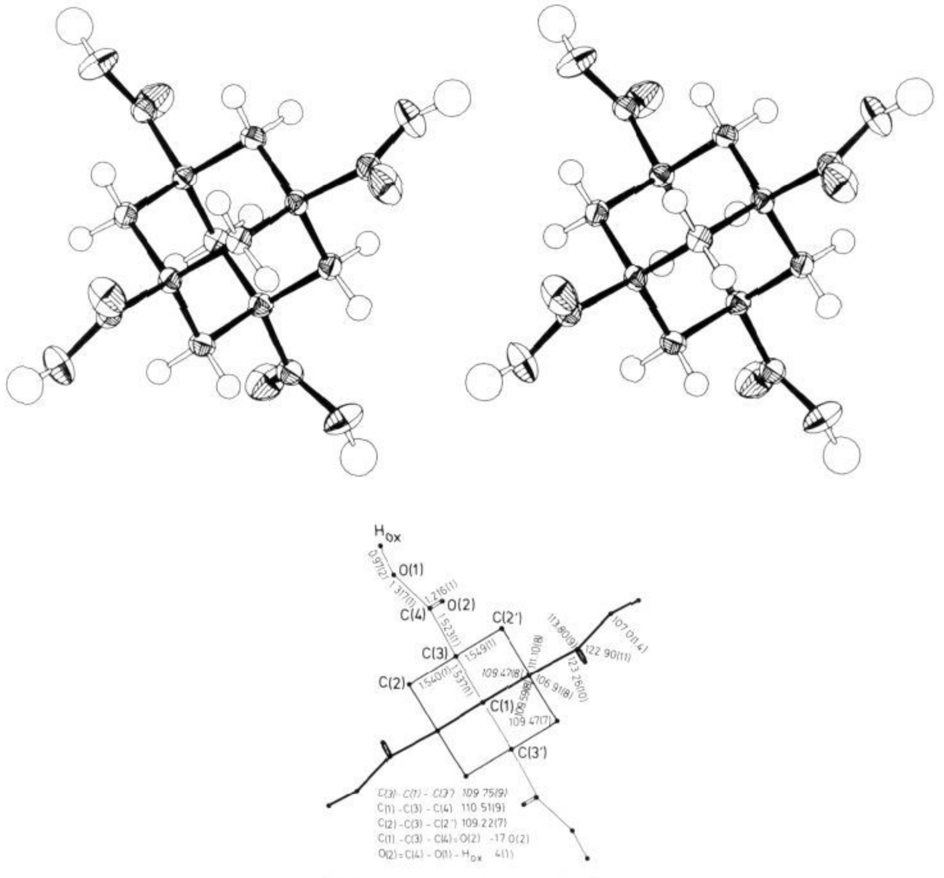

Figure 4. X-ray molecular structure of adamantane-1,3,5,7-tetracarboxylic acid (**1**). Top: stereoview (down the S_4 axis in case of right member of pair) with vibrational ellipsoids (50% probability) for C and O atoms; isotropic temperature factors of H atoms halved. Bottom: atomic numbering, bond lengths (Å), bond angles, and torsion angles (deg) with standard deviations in parentheses.

= 4, crystallographic molecular symmetry S_4; a = 7.510 (5) Å, c = 22.266 (21) Å, V = 1255.80 Å^3; d_{obsd} = 1.651 g cm^{-3}, d_{measd} = 1.65 g cm^{-3} (flotation, CH_2Br_2/acetone); mean refractive index $\bar{n}_D$ = 1.6110 (5);[10] a total of 2375 reflections measured at room temperature (four-circle diffractometer, λ_{Mo} = 0.71069 Å, $\theta_{\max}$ = 36°), of which 1506 independent intensity data remained after averaging; structure solution by direct methods, refinement (C, O anisotropic; H isotropic) including the 1290 reflections with $|F_o| > 3\sigma(F_o)$, R = 0.053, R_w = 0.051; all crystallographic calculations with the program system SHELX76. We thank W. Gebert, Bochum, for collecting the X-ray intensities, and L. Lindenberg for computational help. The final atomic coordinates and temperature factor coefficients are given in Table I. A stereoview of **1** with vibrational ellipsoids as well as relevant geometry data and the atomic numbering is shown in Figure 4. Figures 5–9 illustrate aspects of the diamondoid crystal packing of **1**, which will be discussed in the following section. A list of observed and calculated structure amplitudes has been deposited as supplementary material.

Discussion

The molecules of **1** have S_4 symmetry in the crystal. Expectedly, the rigid adamantane nucleus does not deviate much from T_d

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(10) The tetragonal crystals of **1** are optically uniaxial positive: $n_e^D(\parallel c)$ = 1.6512 (5), $n_o^D(\perp c)$ = 1.5909 (5); $\bar{n}_D$ = (1.6512 + 1.5909 + 1.5909)/3 = 1.6110. These refractive indices were measured by O. Medenbach, Bochum, to whom we extend our appreciation, on a microrefractometer recently designed by himself: Medenbach, O. *Fortschr. Mineral.* **1985**, *63*, 111.

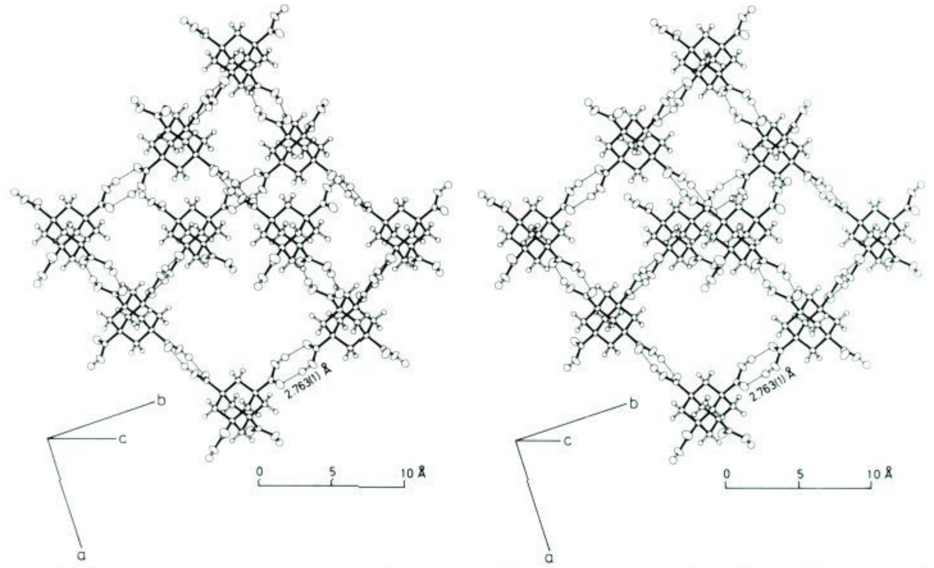


Figure 5. Stereoview of a hydrogen-bonded super-adamantane framework of **1** cut out of an individual diamondoid lattice (with O(H)⋯O distance of the hydrogen bonds). Note the large central cavity, which in the crystal is filled by four interpenetrating equivalent diamondoid frameworks. The view is very roughly along the tetragonal axis *c*, as indicated.

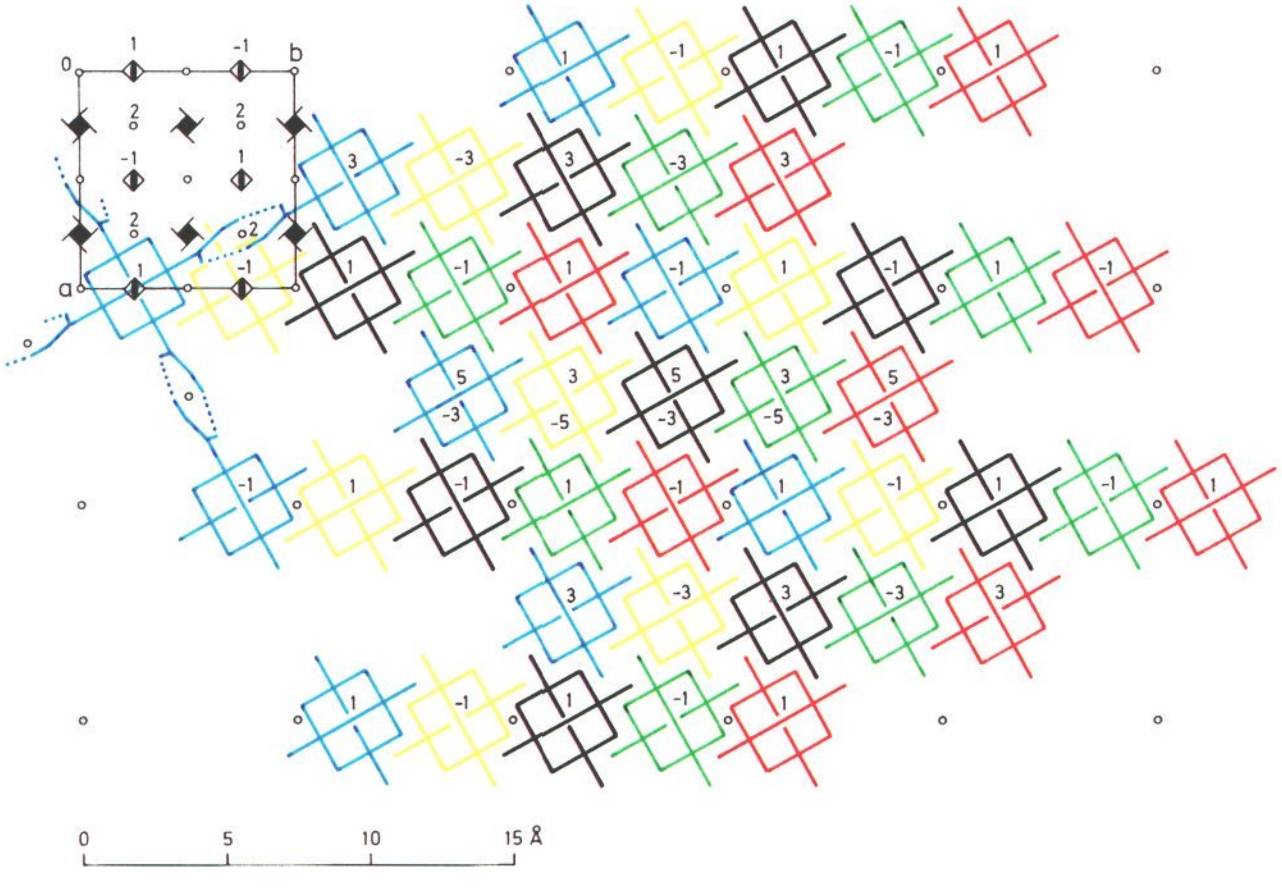


Figure 6. Space group symmetry diagram of **1** projected down the tetragonal axis *c*. Apart from the centers of symmetry defining the origin, the symmetry elements of space group $I4_1/a$ are shown only for one unit cell. Solely carbon frameworks are drawn except for the leftmost (blue) molecule with complete carboxylic groups and the hydrogen bonds emanating therefrom. The elevation of the molecular centers, i.e., of their S_4 axes, is given in units of $c/8$. The five interpenetrating hydrogen-bonded diamondoid lattices are represented by super-adamantane frameworks (Figure 5) for which "olympic" colors have been chosen (see also Figure 8).

symmetry, however. Bond lengths and bond angles are more or less unexceptional besides some small exocyclic angle deformations at the bridgehead carbon atoms (Figure 4). The carboxylic groups are essentially planar, and their conformation with respect to the adamantane framework may be characterized through the C(1)–C(3)–C(4)=O(2) torsion angle of 17.0 (2)°; had this torsion angle the ecliptic value, the structure of **1** would approach the highest possible symmetry D_{2d}. A more closely ecliptic value of

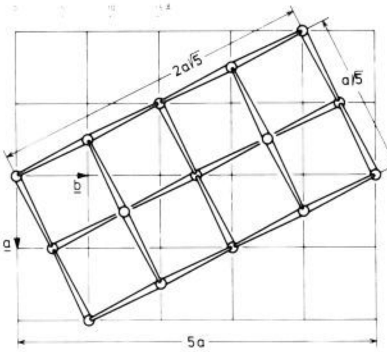
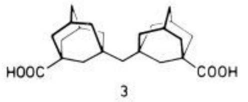


Figure 7. Schematic illustration of the translational equivalence of the five interpenetrating diamondoid lattices in the crystals of **1**, i.e., of the relationship between the translational vector **b** (underlined in the diagram) and the diamondoid lattice geometry; projection down tetragonal axis as in Figure 6; origin shifted by **b**/4. Two fused super-adamantane frameworks cut out of one individual hydrogen-bonded diamondoid lattice are shown in the diagram; the spheres represent the adamantane nuclei at their centers (S_4 axes), while the interconnecting rods stand for the pair-wise doubly hydrogen-bonded carboxylic groups.

8.5 (2)° was measured for the corresponding CCCO torsion angle in crystalline di-1-adamantylmethane-3,3′-dicarboxylic acid (**3**),[11a] whereas the comparable carboxylic groups in bicyclo[2.2.2]octane-1,4-dicarboxylic acid (**4**) avoid ecliptic partial conformations.[11b] These conformational features may be related to the observation that the carboxylic groups of **1** and **3** are essentially ordered in the crystal (see below) while those of **4** are not: In the case of **4** the intramolecular environment of the C—O and C=O bonds of the carboxylic groups is more nearly equivalent than in **1** and **3**. (See ref 1 for a detailed discussion relating to orientational disorder phenomena of this kind in carboxylic acids.)



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As frequently observed in centrosymmetric crystals of carboxylic acids, the molecules of the present adamantane tetracarboxylic acid (**1**) are interlinked by the usual pair-wise hydrogen bonds (Figure 2) across centers of symmetry (Figures 5 and 6). The carboxyl groups do not show orientational disorder (see above) as evidenced by the clearly distinguishable C—O and C=O bond lengths of 1.317 (1) and 1.216 (1) Å, respectively, and the C—C—O and C—C=O angles, which deviate by almost 10° [113.8 (1) and 123.3 (1)°, respectively; Figure 4].[12] It is briefly noted that the hydrogen-bonded carboxyl groups of **1** are neither exactly coplanar nor are their related $C(sp^2)$–$C(sp^3)$ bonds strictly collinear. The respective deviations are significant yet rather small, however, and may in any event not be expected zero simply because of symmetry reasons. This applies similarly for the packing characteristics of many other carboxylic acids. The O(H)···O distances of the hydrogen bonds of **1** amount to 2.763 (1) Å and are thus more than 0.1 Å longer than the normal value of about 2.65 Å.[13] For comparison, the O(H)···O distances of the crystalline dicarboxylic acids **3** and **4** are 2.646 (2) and 2.610 (4) Å, respectively.[11] The comparatively long hydrogen bonds in the crystals of **1** indicate that the diamondoid packing of the tetraacid

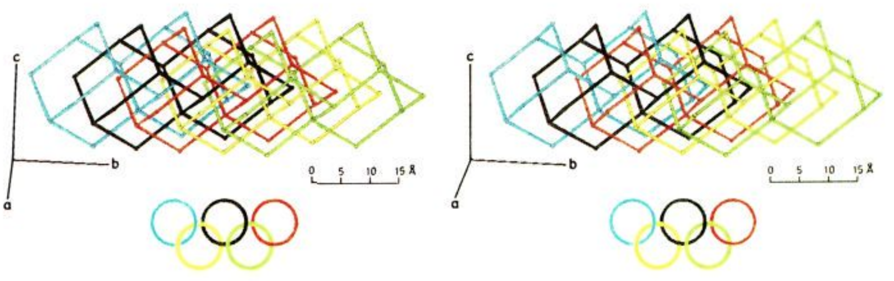

Figure 8. Schematic stereoview of the five interpenetrating hydrogen-bonded diamondoid lattices of **1** represented by pairs of fused super-adamantane frameworks (cf., Figure 7). The translational equivalence of the lattices is clearly evident. The view is very roughly down the axis *a*, as indicated. Spheres and interconnecting rods of the lattices represent adamantane nuclei at their centers (S_4 axes) and interconnecting pairs of doubly hydrogen-bonded carboxylic groups, respectively, as in Figure 7. The choice of colors is highlighted by reproduction of the olympic rings.

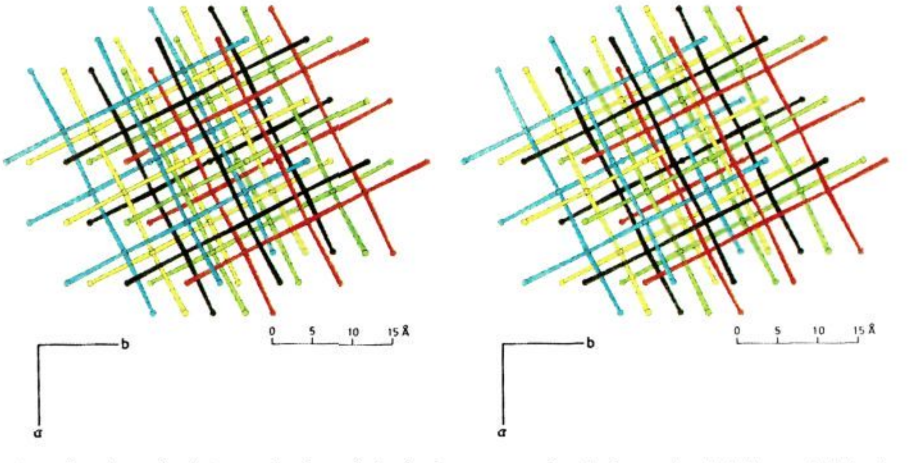

Figure 9. Schematic stereoview along the tetragonal axis *c* of the five interpenetrating hydrogen-bonded diamondoid lattices of **1** represented by super-adamantane frameworks surrounded by belts of 12 additional lattice elements. For further explanations see legend of the analogous Figure 8.

molecules cannot be accomplished entirely without generating some nonbonded strain between the interpenetrating lattices (see below). The crystal structure of **1** would represent an informative test case for crystal force-field calculations[13] both as regards a more detailed understanding of the origin of the observed hydrogen-bond strechings and the quality of the potential functions applied.

In stark contrast to the normal intramolecular structure of **1**, its crystal structure, i.e., the unique three-dimensional arrangement of the tetraacid molecules in space, undoubtedly demands primary attention. It is not easy by means of a simple verbal description to convey an appropriate impression of the intricate crystal packing of **1**. Therefore, the following discussion is supplemented by the three stereodrawings of Figures 5, 8, and 9 and by the geometric symmetry diagrams of Figures 6 and 7.

A "super-adamantane" framework cut out of one super-diamond lattice formed by the hydrogen-bonded adamantane-1,3,5,7-tetracarboxylic acid molecules is shown in Figure 5. The open spaces of this architecture are clearly evident from the drawing and are filled in the crystal by four other symmetry-equivalent super-diamond lattices such that the molecules of **1** may altogether be assigned to five individual diamondoid lattices, which mutually interpenetrate each other yet are unconnected otherwise (fivefold-diamond structure). Hydrogen bonds occur only within a particular diamondoid lattice but not between different lattices. The colored schematic stereodrawings shown in Figures 8 and 9 give a pictorial impression of how the five diamondoid lattices are interwoven, while from the symmetry diagrams of Figures 6 and 7 the spatial relationship between the interlocked lattices may be derived quantitatively.

For the following discussion, let us denote the crystallographic cell-edge vectors of **1** by $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$, and their lengths by a, b, and c, as usual. Since the crystal system is tetragonal, $b = a$, and the cell angles are 90°.

The five interpenetrating diamondoid lattices of **1** are translationally equivalent. The respective translational vector is equal to the cell vector $\mathbf{b}$ (or $\mathbf{a}$), as may be seen from the colored space-group symmetry diagram of Figure 6 (projection down $\mathbf{c}$). For further illustration, in Figure 7 two fused super-adamantane frameworks of one particular diamondoid lattice are shown schematically (projection again down $\mathbf{c}$) whose corners form a rectangle perpendicular to $\mathbf{c}$; the cell edges defined by $\mathbf{a}$ and $\mathbf{b}$ are also outlined. The spheres of the super-adamantane structures of Figure 7 (and similarly of Figure 8 and 9) represent adamantane nuclei, and the interconnecting rods stand for pairs of carboxylic groups linked by pairs of hydrogen bonds (see Figure 5; the super-adamantane frameworks have D_{2d} symmetry). The rectangle just defined is composed of two fused squares such that the long edge is twice the short one. The long edge is defined by the vector $4\mathbf{b}-2\mathbf{a}$, the short one by $\mathbf{b} + 2\mathbf{a}$; the lengths of the edges are thus $2a\sqrt{5}$ and $a\sqrt{5}$, respectively. A diagonal of the rectangle is defined by the sum of these edge vectors, i.e., $5\mathbf{b}$. The translational vector relating the five interpenetrating diamondoid lattices, i.e., $\mathbf{b}$, is therefore seen to be one-fifth of the vector of this diagonal. In simpler words: The individual lattices of the present fivefold-diamond structure are transformed into one another by translating them along the diagonal of a rectangle formed by two fused super-adamantane frameworks as defined in Figure 7; the magnitude of the translation is then necessarily one-fifth of the length of this diagonal.

As noted in the introduction, for simple reasons of molecular symmetry the diamondoid lattices in the crystals of **1** cannot be completely undistorted; i.e., they cannot possess cubic symmetry. At most, tetragonal symmetry can be retained as is actually observed. The diamonoid lattices thus must be either elongated or compressed along the tetrogonal axis c, albeit by a small amount. An obvious choice for defining this distortion is the ratio of the distance between two molecules of **1** sitting on top of each other along the tetragonal axis and interconnected by the vector $\mathbf{c}$ and the distance between an analogous pair of molecules oriented at right angles and interconnected by the vector $3\mathbf{b} + \mathbf{a}$. These are the two nonequilvalent distances between two opposite molecular centers of a super-adamantane framework of D_{2d} symmetry. With the help of Figures 6 and 7 one finds their ratio to be $c/a\sqrt{10} = 0.9376$, indicating a small tetragonal compression. It is noted at this point that the distance r between two neighboring hydrogen-bonded molecules of **1**, estimated at 10.0 Å in the introduction, actually amounts to $r = (^5/_4a^2 + {}^1/_{16}c^2)^{1/2} = 10.074$ Å, as may also be extracted from these illustrations.

The attentive reader will have noticed that the colors attached to the five interlaced diamondoid lattices of **1** in Figures 6, 8, and 9 are not arbitrary yet represent those of the International Olympic Movement. Indeed, the concatenation of the five olympic rings symbolizing the five continents is somewhat reminiscent of the interlocking pattern of the five lattices in the present crystal structure (Figure 8). However, the degree of interpenetration of the fivefold-diamond structure of **1** is much higher than that of the olympic rings.

A substance whose crystal structure is made up of largely undistorted diamondlike lattices may be expected to display a pattern of physical and chemical properties with an underlying tendency toward similarity with the extreme respective behavior of diamond itself. Of course, it is unrealistic to foresee any *pronounced* parallelism of properties between adamantane-1,3,5,7-tetracarboxylic acid (**1**) and diamond given the relatively weak hydrogen bonds and the interpenetration of several unconnected lattices in **1** as compared with the fully covalently bonded single tetrahedral lattice of diamond. As is brought about by the following comparisons, it seems nevertheless justified to a certain limited extent to view properties of **1** in terms of a trend toward diamondlike behavior.

The density and the refractive index of the tetraacid **1** have rather high values for a compound of this composition: $d_{\text{obsd}} = 1.651$ g cm^{-3}, $\bar{n}_D = 1.6110\ (5)$.[10] The extreme respective values of diamond are 3.536 g cm^{-3} and 2.4173. That the interlocking diamondoid lattices of **1** represent a rather favorable architecture like the lattice of diamond itself may be inferred from and correlated with the following observations: (1) The density calculated for **1** from a standard set of atomic increments[14] amounts to only 1.50 g cm^{-3} and is thus significantly lower than the above measured value. (2) It is tolerated that the five interpenetrating hydrogen-bonded diamondoid lattices of **1** fit into each other only with the buildup of strain. Apparently, nonbonded repulsions between the molecules of the different lattices cannot be completely avoided since the hydrogen bonds are stretched such that the O(H)···O distances assume the rather large values of 2.763 (1) Å (see above). (3) The tetraacid **1** has a high melting point beyond ca. 390 °C. At about this temperature the substance does not really melt, however, yet decomposes.[8] Thus, the diamondoid lattices of **1** are so stable (and lead to such a high "true" melting point) that the compound does not experience its melting under normal conditions yet prefers to decompose chemically before its good crystal structure becomes disrupted. Incidentally, this may also be seen in the light of the fact that diamond does not melt under normal pressure yet decomposes on heating above about 1500 °C into graphite, which is thermodynamically slightly more stable. (4) The adamantanetetracarboxylic acid (**1**) was crystallized from an aqueous medium (see the Experimental Section), yet no water molecules were built into the crystal structure, as evidenced by the present detailed X-ray analysis. Thus, the stability of the diamondoid packing of **1** cannot be surpassed by forming a hydrated structure. (5) Finally, the generally poor solubility characteristics of **1**[8] and the relatively low thermal motion in the crystal (Table I, Figure 4) are indicative of a favorable and tight

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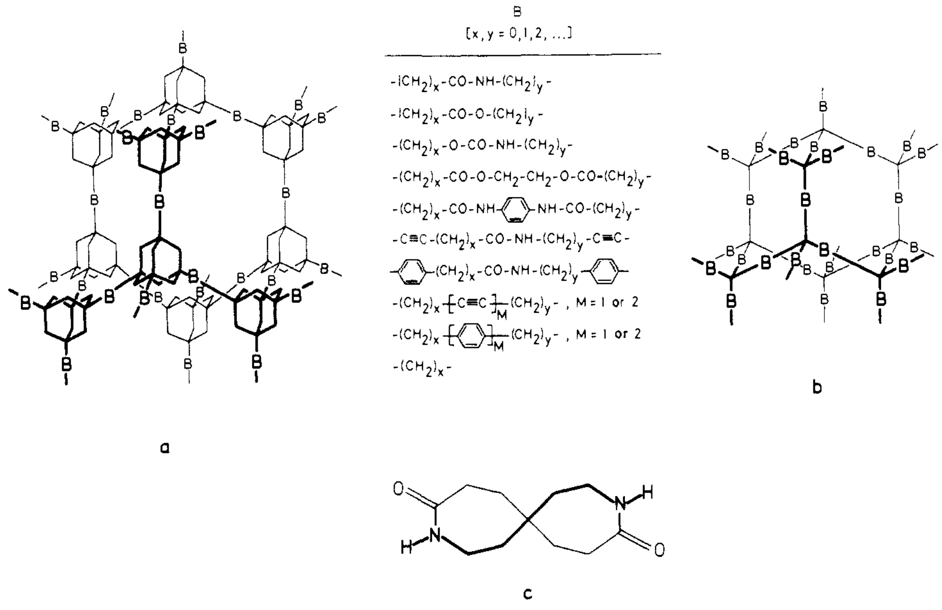


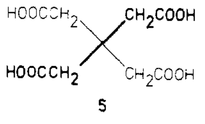
Figure 10. Hypothetical diamondoid polymers based upon (a) 1,3,5,7-tetrafunctional adamantanes and (b) tetrafunctional methanes as monomers. A number of examples of possible bridging elements B interlinking the tetrahedral centers are listed. Except for the last entry B = $-(CH_2)_x-$ with $x < 2$, the actual polymers would consist of interpenetrating three-dimensional diamondoid networks made up of the super-adamantane frameworks shown. The last entry with $x = 0$ corresponds to poly(1,3,5,7-tetradehydroadamantane) (single undistorted diamondoid lattice) and diamond itself, respectively. (c) 3,10-Diazaspiro[6.6]tridecane-4,11-dione, potential (unknown) monomer for a hypothetical nylon-6-type (perlon) diamondoid polyamide ("superlon").

molecular packing. A characteristic property of diamond is its extreme hardness, of course. No attempt was made, however, to consider the hardness of **1** for comparative purposes because of experimental difficulties and the lack of reference data for organic molecular crystals.

Conclusions

The present study shows rather beautifully that tetrafunctional organic molecules with tetrahedrally directed substituents are, under suitable conditions, capable of building in the crystal large hollow diamondlike lattices whose empty spaces are filled by interpenetrating equivalent lattices. Obviously, adamantane-1,3,5,7-tetracarboxylic acid (**1**) is a particularly favorable example considering the rigidity of its carbon skeleton and the almost perfect tetrahedral alignment of the carboxylic groups. As we have seen, this in turn leads to relatively little distorted hydrogen-bonded super-diamond (diamondoid) lattices mutually interpenetrating each other. The present study invites one to look for other modes and degrees (multiplicities) of interpenetration of diamondoid lattices by varying in a systematic way the structural–chemical possibilities conceivable in this context. Clearly, tetracarboxylic acids are particularly attractive for this sort of tailoring of intermolecular architectures, yet differing functionalizations capable of furnishing suitable hydrogen bonding or other charge interactions may also be envisaged.[15]

As a first step toward a more systematic exploration of packing modes of tetracarboxylic acids with tetrahedrally oriented carboxyl groups, we have in the meantime measured the crystal structure of methanetetraacetic acid (**5**).[16] The structural preconditions



5

for forming diamondoid lattices are in this case less straightforward than for **1** because the carboxylic groups in **5** do not emanate tetrahedrally from a common point and because **5** is a conformationally more flexible molecule than **1**. Notwithstanding these seemingly less favorable characteristics, **5** again turns out to set up hydrogen-bonded hollow diamondoid lattices (tetragonally elongated) whose empty spaces are filled by interpenetrating equivalent lattices. The degree (multiplicity) of interpenetration is threefold this time, such that **5** has a distorted triple-diamond crystal structure.[17]

The present X-ray analysis of adamantane-1,3,5,7-tetracarboxylic acid (**1**) leads to two potentially useful implications, the first of which concerns the possible formation of a novel type of solid-state host–guest inclusion compounds. The cavity of a hydrogen-bonded super-adamantane framework of **1** corresponds to a sphere roughly 12 Å in diameter such that the accommodation of even large guest molecules could be envisaged. As described above, the large empty spaces in the diamondoid lattices of **1** are filled by interpenetrating equivalent lattices. In a way, the tetracarboxylic acid **1** may therefore be viewed as a sort of self-inclusion compound. Since the five individual diamondoid lattices of **1** are tightly interlocked (cf., the high density discussed above), it is unlikely that guest molecules may be accommodated by **1** without lowering the degree of interpenetration. Guest complexation could thus possibly be accomplished by relatively empty quadruple- or triple-diamond structures of **1**. Similar considerations apply to methanetetraacetic acid (**5**) regarding its role as a potential host for inclusion compounds. The structural study referred to above of a series of tetracarboxylic acids with tetrahedrally directed carboxyl groups displaying varying modes and degrees of interpenetration of diamondoid lattices seems indicated in particular in order to establish a body of structural references for systematically probing the guest-complexation potentialities of such systems. It is noted that trimesic acid (**2**), the two-dimensional analogue of **1**, does indeed form inclusion compounds within a structure consisting of interpenetrating planar super-

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[15] It is noted that the crystal structure of the tetraamide of adamantane-1,3,5,7-tetracarboxylic acid **1** may be described in terms of four distorted interpenetrating hydrogen-bonded diamondoid lattices as we have observed in the course of a recent X-ray analysis: Ermer, O., unpublished results. However, in the crystal structure of the tetraamide different interlocking diamondoid lattices are connected by additional hydrogen bonds unlike in **1** (distorted, cross-linked fourfold-diamond structure).

[16] Ermer, O.; Eling, A. *Angew. Chem., Int. Ed. Engl.*, in press.

[17] For comparison with **5**, the crystal structure of pentaerythritol, $C(CH_2OH)_4$, appears to be of interest. This tetraalcohol also crystallizes tetragonally yet does not form diamondoid lattices. Presumably, this is at least partly due to the less suitable directionality of the hydrogen bonds of pentaerythritol as suggested by model considerations. Numerous crystallographic studies on pentaerythritol have been reported; see, e.g.: (a) Eilerman, D.; Rudman, R. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1979**, *B35*, 2458. (b) Llewellyn, F. J.; Cox, E. G.; Goodwin, T. H. *J. Chem. Soc.* **1937**, 883.

graphite networks.[18]

The second implication of the present study concerns the speculative design of a novel type of polymers with potentially extreme properties for which the crystal structure of **1** provides a model. The interlocking diamondoid lattices of **1** may be viewed as weakly (hydrogen-) bonded crystalline polymers with an extremely high degree of three-dimensional cross-linking. By analogy, the ultrastrong diamond itself may be looked upon as a tightly (covalently) bonded crystalline polymer three-dimensionally maximally cross-linked. The role of the monomers in the two cases is played by the individual molecules of **1** and the carbon atoms, respectively. Replacing the weak hydrogen bonds in **1** by chains of covalent bonds would lead to more conventional novel polymers consisting of interpenetrating firmly bonded diamondoid networks ("diamondoid polymers"). Consequently, diamondoid properties such as extremely high strength, modulus and hardness, high refractive index and density, as well as extreme thermal stability and chemical inertness, could be foreseen for such hypothetical polymers. Moreover, diamondoid polymers would be expected to represent high-performance polymers with *isotropic* extreme properties in contradistinction to linear fibrous high-performance polymers such as aromatic polyamides (aramid fibers, Kevlar), which display extreme properties only *anisotropically*, i.e., parallel to the (fiber) axis of polymerization.

Figure 10a shows some hypothetical possibilities of constructing diamondoid polymers based upon 1,3,5,7-tetrafunctional adamantanes. For example, a diamondoid polyamide ("nylamant") would result through replacing the pairs of hydrogen bonds and carboxylic groups interlinking the adamantane nuclei of **1** by the covalent bridging chain $B = -(CH_2)_xCONH(CH_2)_y-$ with $x, y = 0, 1, 2, ...$[19] Similarly, hypothetical diamondoid polymers may be designed on the basis of tetrafunctional methanes (Figure 10b). The spirobis(lactam) shown in Figure 10c (a double ϵ-caprolactam) would, for instance, represent an attractive monomer for generating a nylon-6-type (perlon) diamondoid polyamide ("superlon"). This spirobis(lactam) is unknown yet should be readily obtainable from the known dioxime[20b] of spiro[5.5]undecane-3,9-dione.[20,21]

Whether diamondoid polymers of the type outlined briefly above can actually be made, or whether they are merely hypothetical concoctions of no practical use, is open to speculation. An ordered diamondoid polymerization of the tetrafunctional monomers is statistically/entropically a rather unfavorable process. In addition, crystalline diamondoid polymers are expected to display poor solubility properties and will not exist in the melt. The prospects for realizing highly ordered crystalline diamondoid polymers with interpenetrating three-dimensional lattices are therefore rather unfavorable unless suitable special polymerization techniques can be found. Possibly, less ordered glasslike polymeric structures formed in the primary polymerization process can be made to rearrange to thermodynamically more favorable crystalline diamondoid architectures of higher order by (catalytic) equilibration and annealing procedures at elevated temperatures.[22]

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Registry No. 1, 100884-80-8.

Supplementary Material Available: List of observed and calculated X-ray structure amplitudes of **1** (6 pages). Ordering information is given on any current masthead page.

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(19) A diamondoid polymeric hydrocarbon made up of adamantane cores with directly covalently linked bridgehead carbon atoms is also conceivable [poly(1,3,5,7-tetradehydroadamantane); last entry of Figure 10a, $x = 0$]. For a structure of this sort with a single undistorted diamondoid lattice, which would suffer from severe nonbonded H···H repulsions, a density of about 1.37 g cm^{-3} may be estimated ($r = 4.70$ Å).[5]

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(21) On first thought, one would expect the spirobis(lactam) of Figure 10c to form chains of doubly hydrogen-bonded molecules in the crystal. However, a distorted diamondoid crystal structure appears also possible provided neighboring molecules are linked by single rather than pair-wise hydrogen bonds. Diamondoid crystal packing could perhaps help favor diamondoid polymerization of the spirobis(lactam). Experimental work is pursued.

(22) We thank G. Wegner, Mainz, for a discussion (Nov 4, 1986) concerning the prospects of realizing diamondoid polymers.

Homogeneous Gas-Phase Formation and Destruction of Anthranil from *o*-Nitrotoluene Decomposition

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Abstract: Dilute quantities of *o*-nitrotoluene and anthranil have been pyrolyzed in comparative rate single pulse shock tube experiments. Rather than $C-NO_2$ bond cleavage and NO_2 isomerization found as major channels in *p*-nitrotoluene decomposition, we demonstrate that the important pathway for pyrolysis involves the formation of anthranil with the following overall rate expression: $k(o\text{-nitrotoluene} \rightarrow \text{anthranil}) = 1.2 \times 10^{13} \exp(-26020/T)/\text{s}$. The anthranil that is formed is very unstable under our conditions; the rate expression for disappearance has been found to be the following: $k(\text{anthranil})_d = 3.7 \times 10^{15} \exp(-25800/T)/\text{s}$. Arguments are presented that suggest that the first rate expression is representative of a retroene reaction and the second expression is for the breaking of the N-O bond in anthranil. These conclusions emphasize the difference in results from shock tube and laser pyrolysis experiments. Their implications on the initiation reactions in the decomposition of nitroaromatic explosives are discussed.

In an earlier study on the decomposition of *o*-nitrotoluene[1] under single pulse shock tube conditions, we found that only one-third of the lost reactant could be accounted for in terms of products from an initial $C-NO_2$ bond split. This is in striking contrast to the situation for nitrobenzene or *p*-nitrotoluene where over two-thirds of the products are accounted for in this manner and the remainder could be reasonably interpreted in terms of an isomerization of the nitro compound to the nitrite. At that time we were not able to identify the principal channel for *o*-nitrotoluene

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