Distorted Fivefold-Diamond Structure of 4,4-Bis(2-carboxyethyl)pimelic Acid ('Methanetetrapropionic Acid')

by **Otto Ermer***, **Andreas Kusch**, and **Christof Röbke**

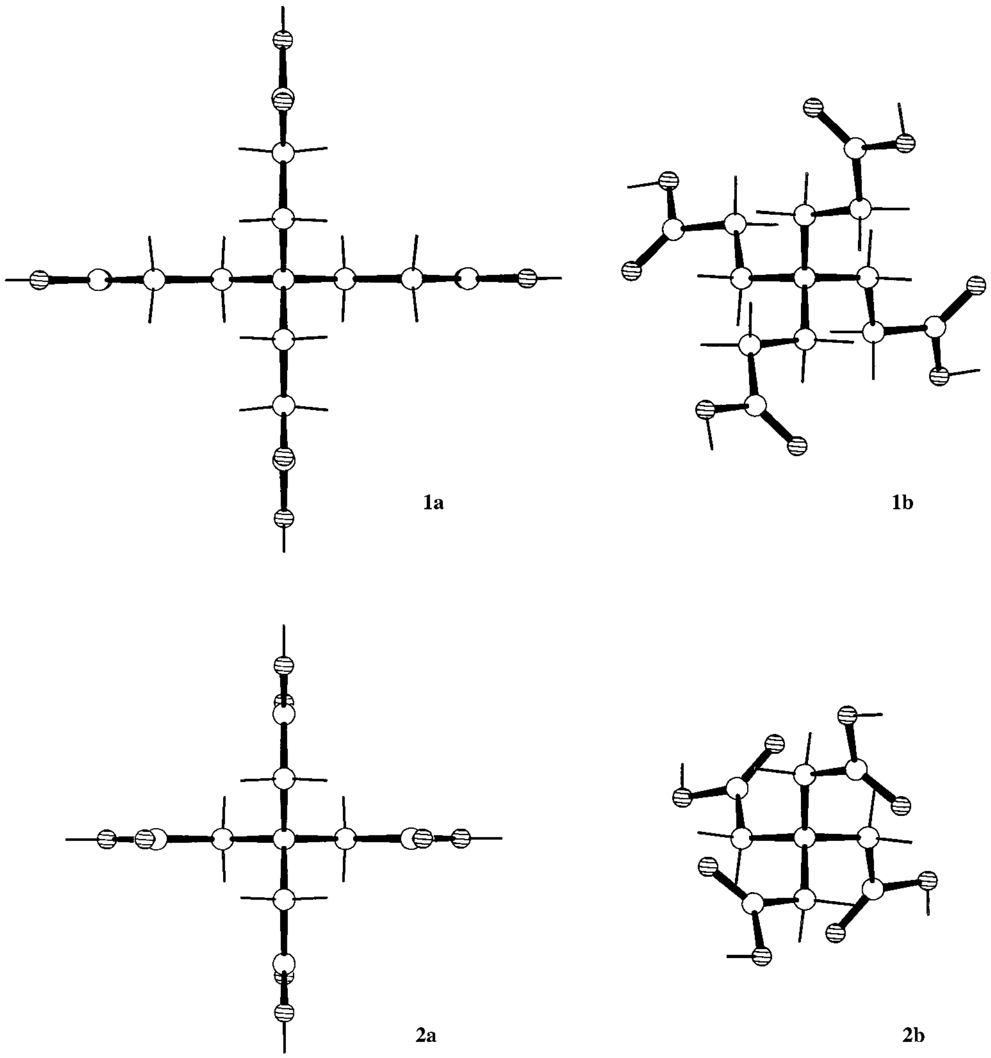
Institut für Organische Chemie der Universität, Greinstrasse 4, D-50939 Köln

Dedicated to Professor *Jack D. Dunitz* on the occasion of his 80th birthday

The molecules of 4,4-bis(2-carboxyethyl)pimelic acid (=4,4-bis(2-carboxyethyl)heptanedioic acid; **1**) assemble to build up hollow, five-fold interpenetrating diamond-like networks in tetragonal crystals *via* standard pairwise H-bonds between the carboxy groups. In keeping with the flat, extended molecular conformation of **1** of approximate D_{2d} symmetry, the supramolecular diamondoid networks are tetragonally compressed. Their mode of interpenetration is unusual and corresponds to that of adamantane-1,3,5,7-tetracarboxylic acid, which has an undistorted five-fold diamond structure. Both the degree and the mode of interpenetration of **1** differ from those of the lower homologue 3,3-bis(carboxymethyl)glutaric acid (**2**), which adopts a more-common tetragonally elongated triple-diamond architecture in the solid state.

Introduction. – Recent renewed interest in diamond-like interpenetration patterns of supramolecular solid-state architectures [1] prompts us to report the crystal structure of 4,4-bis(2-carboxyethyl)pimelic acid (=4,4-bis(2-carboxyethyl)heptanedioic acid, 'methanetetrapropionic acid'; $C(CH_2CH_2COOH)_4$; **1**). This structure was uncovered by X-ray diffraction in our laboratory rather long ago [2], but remained unpublished ever since, as we deemed it sufficient at the time to make available in the literature as a prototypal model only the crystal structure of the smallest chemically stable member of this class of tetracarboxylic acids, *i.e.*, of 3,3-bis(carboxymethyl)glutaric acid ('methanetetraacetic acid'; $C(CH_2COOH)_4$; **2**) [3]. In the crystals of **2**, a distorted triple-diamond architecture is set up *via* standard pairwise H-bonds between the carboxylic groups. Provided diamondoid networks are formed in the crystals of **1**, too, a higher degree of interpenetration is clearly to be expected, due to the four extended side arms of the molecule, as compared to **2**.

Within staggered partial conformations around the $C(sp^3)-C(sp^3)$ bonds, six more symmetric forms of **1** may, in particular, be considered, which have the carboxy groups tetrahedrally directed, as required for diamondoid assembly. Detailed conformational analysis shows that only the tetragonally compressed, rather flat conformation **1a** of D_{2d} symmetry, and the tetragonally more-elongated and more-compact form **1b** of S_4 symmetry have to be taken into account (*Fig. 1*). Conformers **1a** and **1b** have the $C-CH_2-CH_2-C$ torsion angles antiplanar (180°) and nearly antiplanar, respectively, whereas, in the remaining four tetrahedral conformations of S_4 and D_2 symmetry, these dihedral angles adopt rather more-synclinal (*ca.* 60°) values. Force-field calculations (MM3, gas phase) indicate that **1a** and **1b** are energetically more favorable by at least *ca.* 8 kcal mol^{-1} than the other four tetrahedral forms, which suffer from more-severe



1a **1b**

2a **2b**

Fig. 1. *Favorable tetrahedral conformations of* **1** *and* **2**. Diagrams based on force-field-optimized geometries; crystal conformations of **1** and **2** essentially correspond to **1a** and **2b**, respectively.

gauche interactions. Furthermore, these calculations render **1a** and **1b** practically equi-energetic within 0.1 kcal mol^{-1}. Fully analogous to **1**, 'methanetetraacetic acid' (**2**) involves also two favorable tetrahedral conformations: a tetragonally compressed form **2a** (D_{2d} symmetry) and a more-elongated form **2b** (S_4 symmetry). Force-field calculations also render **2a** and **2b** almost equi-energetic within 0.3 kcal mol^{-1}. According to the calculations, the conformations **1a**,**b** and **2a**,**b** correspond to shallow potential-energy minima, partly due to the facile torsions of the carboxy groups around the C(sp^3)–C(sp^2) bonds[1].

Results and Discussion. – 'Methanetetrapropionic acid' (**1**) was synthesized by homologation of 'methanetetraacetic acid' (**2**) *via* a 35-year old literature protocol [4]; **2** was obtained according to an 80-year old procedure [5]. Large crystals of **1** of distorted octahedral shape could be easily grown from H_2O. These crystals adopt the tetragonal space group $I4_1/a$ with four molecules in the unit cell[2]. From this, S_4 molecular symmetry follows. However, the higher symmetry D_{2d} is fairly well-approximated, and the molecules of **1** take up a conformation similar to that of **1a** in the crystal. The carboxy groups are statistically twofold orientationally (or rather conformationally) disordered through torsions around the C(sp^3)–C(sp^2) bonds (*Fig. 2*), and, concomitantly, the O-atoms show excessive thermal motion[2]. It is noted that 'methanetetraacetic acid' (**2**) also crystallizes in space group $I4_1/a$ with four molecules in the cell [3]. The ensuing molecular conformation of S_4 symmetry of **2** in the crystal does not correspond, however, to the type of **1a**, but rather follows the central structural pattern of **1b**. Thus, it is seen that, in the crystal, **1** is taking up the tetragonally compressed conformation **1a**, while **2** adopts the rather more tetragonally elongated structure **2b**.

Similar to **2**, the molecules of **1** join to form large and porous distorted diamond-like networks in the crystal *via* standard pairwise H-bonds between the carboxy groups extending across centers of symmetry (*Fig. 3*). The O···O distances of the inter-carboxylic H-bonds corresponding to both disordered carboxy orientations assume the normal values 2.63(1) and 2.65(1) Å, respectively. Notwithstanding the identical connectivities of the individual H-bonded diamondoid networks of both tetraacids, the nature of the distortions relative to ideal tetrahedral directionalities is different in both cases. In keeping with the tetragonally compressed molecular conformation of **1**, the

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[1] Within MM3, **2a**, in fact, corresponds to an extremely shallow transition state (one very low imaginary vibrational frequency) and the true minimum has only D_2 symmetry. However, the latter is lower in energy than **2a** by merely 0.02 kcal mol^{-1} and deviates structurally only very slightly and insignificantly from D_{2d} symmetry.

[2] Large distorted octahedral crystals of **1** from H_2O, m.p. 264°; space group $I4_1/a$ (No. 88), $Z = 4$, $a = 9.4640(4)$, $c = 17.7726(7)$ Å; $d_x = 1.270$, $d_m = 1.28$ g cm^{-3}; crystallographic molecular symmetry, S_4. The X-ray intensities were originally measured sequentially on a four-circle diffractometer with a conventional scintillation counter, and, more recently, on a similar diffractometer equipped with a *CCD* area detector, by Mo radiation ($\lambda = 0.71073$ Å). A crystal measuring *ca.* $0.8 \times 0.5 \times 0.5$ mm^3 was used. All results presented herein are based on the more-recent measurements (room temperature). Structure solution by direct methods (SHELXS97); the carboxyl groups were found to be orientationally twofold disordered, and initial refinements showed that, within experimental error, the statistical weights of both carboxyl orientations are about equal. In subsequent refinements (SHELXL97), the weights were accordingly fixed at the ratio 0.5:0.5. Final residuals, $R1 = 0.061$ including 1253 reflections with $F_o > 4\sigma(F_o)$, $wR2 = 0.182$ including all measured 1781 independent reflections ($R_{int} = 0.038$); maximum residual electron density, $\Delta\rho_{max} = 0.20$ eÅ^{-3}. For comparison, a refinement with a single average carboxyl orientation gave the markedly higher residuals $R1 = 0.108$, $wR2 = 0.350$, and $\Delta\rho_{max} = 0.70$ eÅ^{-3}. A low-temperature measurement was attempted at 100 K. However, the diffraction data obtained were of deteriorated quality, and no detailed structural information could be derived; possibly a phase transition interferes. *CCDC* No. 192554 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from *Cambridge Crystallographic Data Centre*, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc. cam.ac.uk).

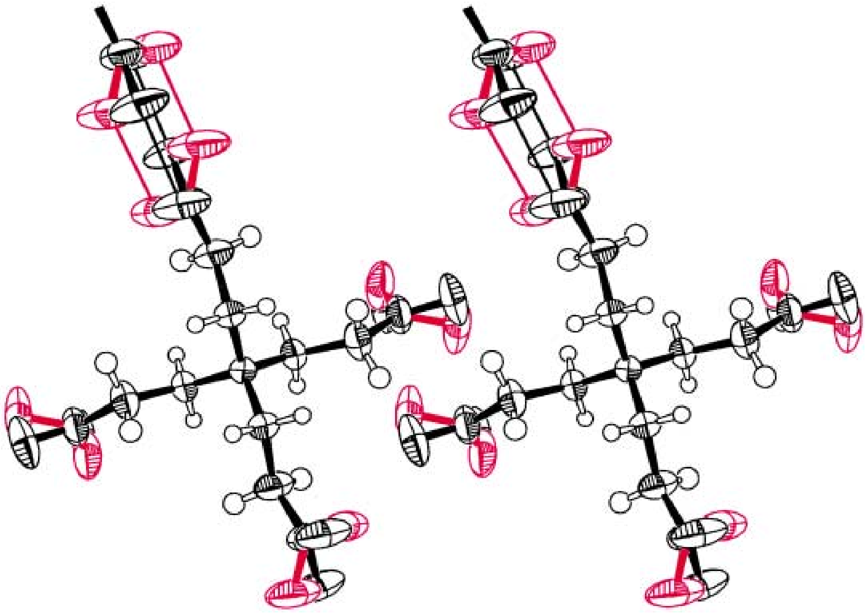

Fig. 2. *Stereoview along the* S_4 axis (right-hand member of pair) *of isolated molecule of* **1** *in the crystal with vibrational ellipsoids* (50% probability; isotropic temperature factors of H divided by 4). The two disordered carboxyl orientations are highlighted by color; they differ by a torsion around the C(sp^3)–C(sp^2) bonds of 32°; hydroxy O-atoms of the carboxyl groups peripheral; C–O and C=O lengths of both orientations 1.306, 1.300, and 1.224, 1.186 Å, respectively (average standard deviation, 0.006 Å); carboxyl H-atoms omitted, since only the average position could be refined. For the top carboxyl group, the H-bonded companion of a partner molecule is also shown.

supramolecular diamond frameworks are also severely compressed tetragonally (compression factor 0.5939; *Fig. 3*). On the other hand, in the crystals of the lower homologue **2** with its tetragonally more-elongated molecular conformation, the supramolecular diamond nets are correspondingly distinctly elongated (elongation factor 1.6914) [3]. Thus, the extent of distortion from tetrahedral disposition of both diamond-like networks is about the same.

The spacious cavities of the individual diamond-like networks of **1** are filled by interpenetration of altogether five symmetry-equivalent networks (*Fig. 4*). However, the packing efficiency is not particularly high, as evidenced by the rather small crystal density of 1.28 g cm^{-3}[2]). This relatively loose crystal packing is also mirrored through the disorder of the carboxy groups, which, thus, apparently have ample room at their command in the molecular fabric. Obviously, the distance between the centers of two doubly H-bonded molecules of **1** is considerably longer than in the crystals of the smaller homologue **2** (11.476 *vs.* 8.761 Å). Accordingly, the degree of diamond-like interpenetration of **1** (five-fold) is higher than that of the lower homologue **2** (three-fold). More interesting is the observation that the mode of interpenetration differs in both cases, too: in the crystals of 'methanetetraacetic acid' (**2**), the individual H-bonded diamond-like frameworks are translationally equivalent and may be merged

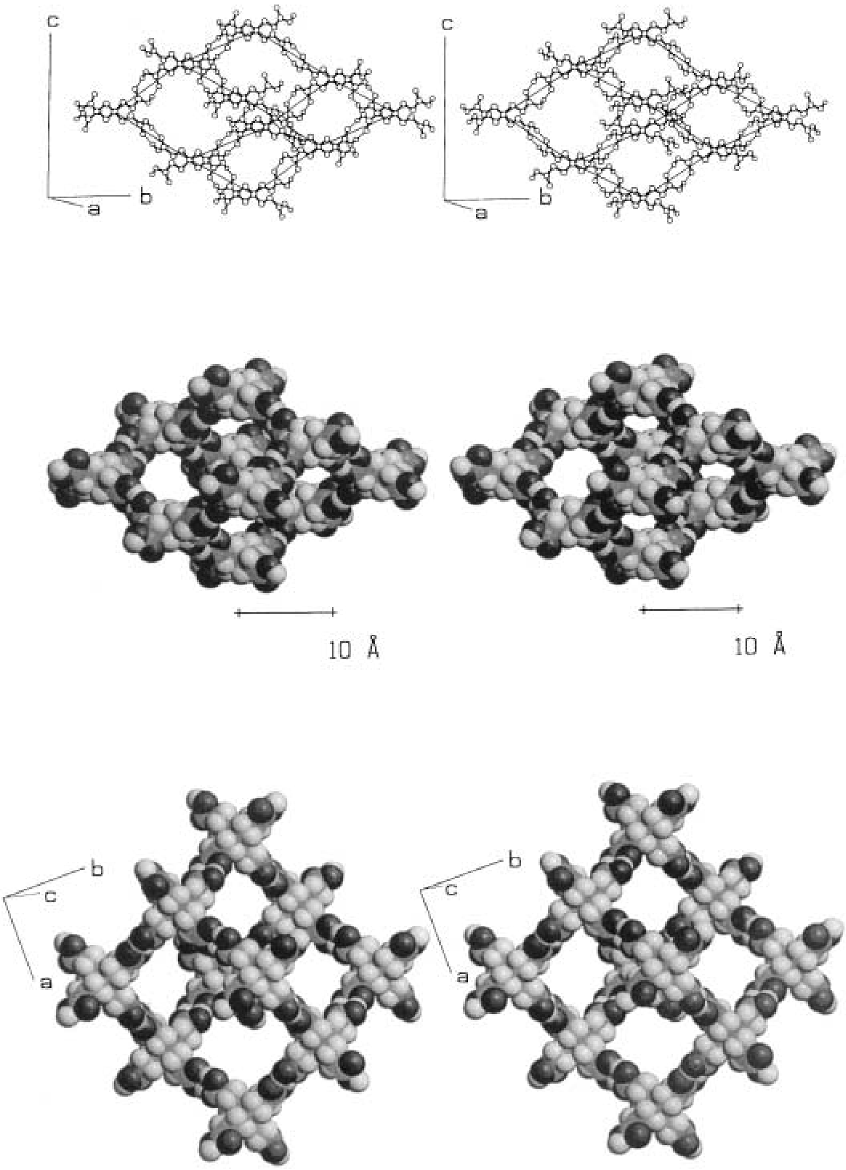

Fig. 3. *Stereoviews of a H-bonded superadamantane unit of* **1** *as cut out of a single diamond network. Top and middle:* Ball-and-stick and space-filling representations viewed essentially perpendicular to the tetragonal *c* axis; note the tetragonal compression of the network. *Bottom:* Space-filling view essentially along the *c* axis. Averaged carboxy orientations drawn; H-atoms in the top diagram omitted except for carboxy groups.

into one another by shifting them by one third of a vector interconnecting two opposite tetrahedral molecular centers of a super-adamantane building block. In the case of **2**, this merging translation corresponds to the tetragonal cell edge *c* along which the diamond-like networks are elongated [3]. Many other examples of multiple diamond structures have been uncovered in the recent past, following this mode of interpenetration, which may thus be referred to as the common or standard interpenetration pattern of such concatenated architecture [1]. In the present, rather exceptional case of 'methanetetrapropionic acid' (**1**), the five interlocked, distorted diamond networks are also translationally equivalent, but the merging translation does not occur along a vector linking opposite tetrahedral centers of a super-adamantane unit. Rather, the merging translation corresponds to one fifth of a vector perpendicular to the tetragonal cell edge *c*, which represents a diagonal of a rectangle formed by four coplanar tetrahedral molecular centers of two fused super-adamantane units as shown in *Fig. 4*. The ratio of the two different edges of this rectangle is 2 : 1. As is also evident from *Fig. 4*, the diamond-like merging translation in the crystals of **1** coincides with the crystallographic elementary translations *a* and *b*, respectively.

The question arises as to *why* the diamond-like interpenetration modes of **1** and **2** differ despite the chemical similarity of the two homologous compounds. While a full answer to this problem is not obvious, it may, nevertheless, be concluded that, within the tetragonally compressed molecular conformation of 'methanetetrapropionic acid', **1a**, and the ensuing tetragonally compressed diamond-like networks in the crystal, a five-fold interpenetration (as required in order to satisfy the observed crystal density) in a standard mode analogous to that in **2** can be ruled out simply due to the steric bulk of **1a**. This holds for both a merging translation along the tetragonal axis *c* or perpendicular to it, as evidenced by inspection of space-filling molecular models. On the other hand, a standard interpenetration mode analogous to that of **2** could possibly be realized also in the case of **1** if the latter were to take up the alternative favorable molecular conformation **1b**, which is tetragonally more-elongated and corresponds to an extended version of the conformation adopted by **2** in its crystals. An interlaced, tetragonally elongated multiple diamond architecture of **1** of this type would, however, have to cope with hollow channels along the 4_1 screw axes due to the longer side arms of **1** as compared to **2**. Thus, it would appear that, in the crystals of **1**, the tetragonally compressed molecular conformation **1a** is favored over the more-elongated form **1b**, since only by adopting conformation **1a** may a satisfactory multiple-diamond architecture be set up, but, indeed, with the observed unusual mode of interpenetration.

The mode of interpenetration of the five translationally equivalent H-bonded diamond-like lattices as occurring in the crystals of 'methanetetrapropionic acid' (**1**), in fact, turns out to be rare, and only one other known example may be cited, *i.e.*, the beautiful five-fold diamond architecture of adamantane-1,3,5,7-tetracarboxylic acid [6]. These two crystal structures agree in every crystallographic respect; the only difference of the supramolecular architectures concerns the tetrahedral alignment of the tetraacid molecules in the two cases: while, in **1**, as noted, the individual diamond frameworks are tetragonally compressed, those of the adamantane-tetracarboxylic acid are almost undistorted. However, it is pointed out in conclusion that it makes sense to refer to the present mode of interpenetration of **1** and of the adamantane-tetracarboxylic acid as unusual only when if one takes into account *any arbitrary* degree of interpenetration (number of interpenetrating diamond lattices). If, on the other hand, the discussion is restricted to five-fold diamond structures alone, then the present interpenetration mode as adopted by **1** and the adamantane-tetracarboxylic

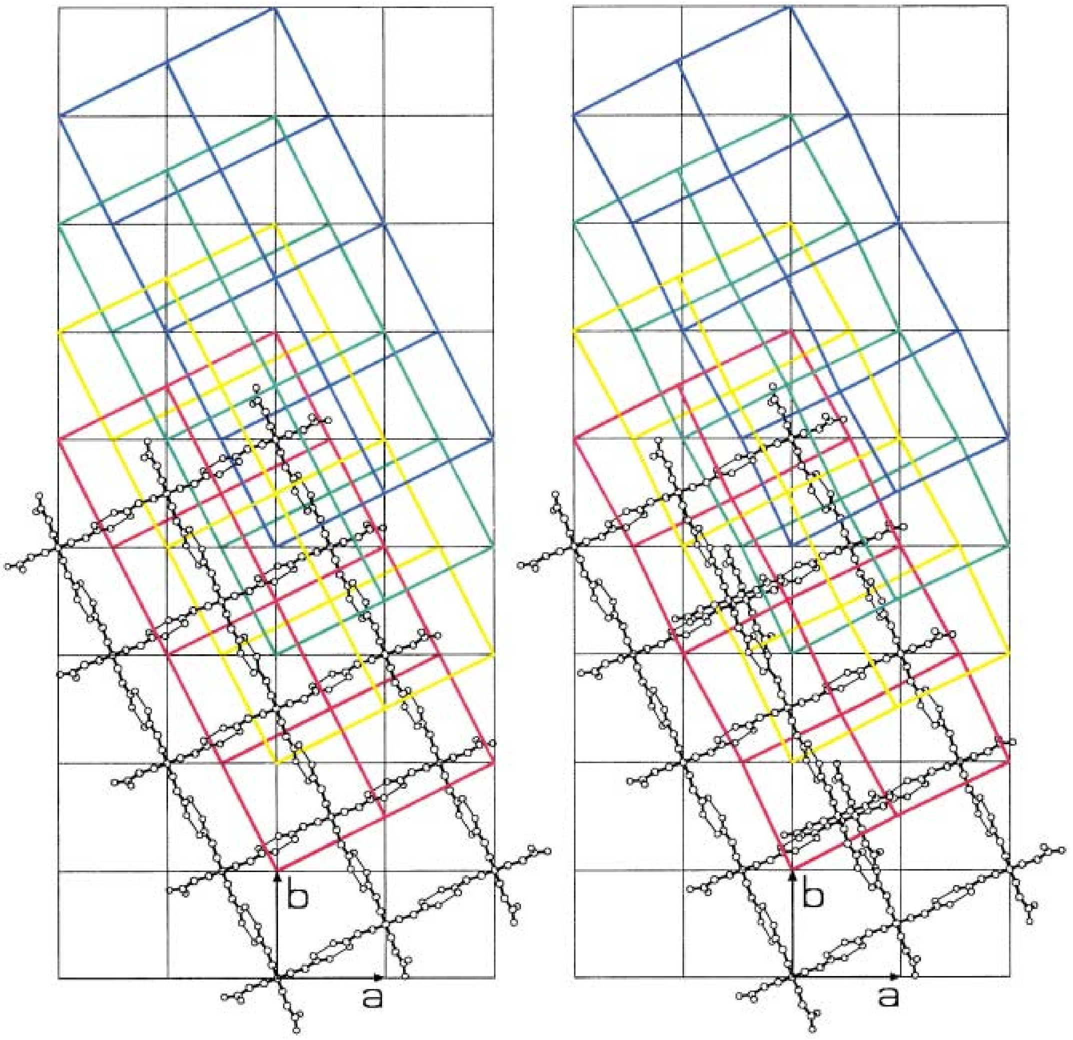

Fig. 4. *Stereoview of the interpenetration mode of the five-fold diamond structure of* **1**. Each diamond network is represented by two fused superadamantane units, of which one is drawn in full (*black*; averaged carboxy orientations, H atoms omitted), while the remaining four (*colored*) are mapped out diagrammatically only by straight lines joining the centers of the tetrahedral building blocks of the lattices, *i.e.*, the H-bonded tetraacid molecules. For the left-hand member of the stereopair, the view is exactly down the tetragonal c axis. Note the translational equivalence of the five diamond lattices along cell edge vector **b** in the diagram, and *cf.* [6] for more details of this interpenetration mode.

acid represents a fully valid alternative possibility compared to the standard mode, and there is no obvious reason to, *a priori*, prefer one mode over the other. Which mode is ultimately chosen in this case depends on the individual chemical, structural, and steric properties of the specific tetrahedral molecular building blocks (as well as of bifunctional linkers, and possible counter ions or guest species) giving rise to the five interlocked diamond networks. Indeed, yet another rather intricate mode of interpenetration has recently been uncovered in a severely distorted five-fold diamond structure of low symmetry taken up by a tetrahedral Cu^I coordination polymer with dipyridylethylene linkers [1b].

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