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# Nonparallel Chain Axes in Polymeric Molecular Crystals

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ABSTRACT: The crystal structure of two semiflexible dicarboxylic acids forming chains is reported; these compounds are models for the crystal packing of polyesters based on 1,5- or 2,7-dihydroxynaphthalene and aliphatic dicarboxilic acids and, more generally, for crystal packing of semiflexible chains containing conformationally blocked aromatic cores along the chain. In both crystal structures, chain axes are not parallel to each other, this unusual feature being connected, seemingly, with the lateral packing of aromatic cores present in the molecules.

## Introduction

Dicarboxylic acids are good model compounds for the crystal structure of linear polymers. They have been studied as model compounds of stereoregular polyolefins (e.g., *meso* and *racemic* 2,4-dimethylglutaric acids for isotactic and syndiotactic polypropylene, respectively)[1−3] and of main chain liquid crystalline semiflexible polymers.[4]

Crystal packing of these compounds is characterized by formation of extended rows of molecules held together by a hydrogen bond between carboxylic groups (cyclic hydrogen bonded dimers),[5] thus simulating the long covalent chains of a true linear polymer. These rows of molecules, as well as the chains of a crystalline polymer, have translational symmetry; therefore the Bravais lattice of the crystal must have (at least) one vector equal to the vector of translational repetition of the chain.

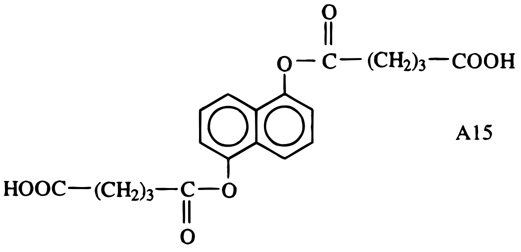
Another feature observed in the crystal structure of polymers and of dicarboxylic acids forming rows, so that it stays as a basic postulate of polymer crystallography, is the parallelism of chain axes. Actually, this feature is not imposed by the symmetry and exceptions may be possible in principle.

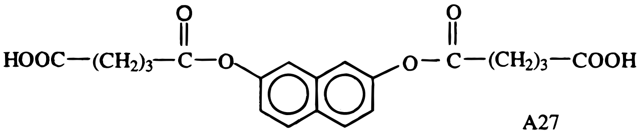
In the field of polymers the only known exception to the rule of chain axes parallelism is the crystal structure of the $\gamma$ form of isotactic polypropylene,[6] while no exception has been observed to date for dicarboxylic acids forming rows.

In the last years we have been studying the crystal structure of several $\alpha-\omega$ dicarboxylic acids containing a mesogenic core, as solid-state model compounds of main chain semiflexible liquid crystalline polymers.[7−9] Mesogenic cores have been considered that are present in some of the most common main chain liquid crystalline polymers (e.g., 4,4′-biphenyl, *p*,*p*′-bis(acetophenon)azine). In these structures a parallel packing of molecular rows having linear symmetry *t*1 or *t*i has always been found.[10] In particular, parallelism of chain axes was also observed in the rather unusual case of rows of different symmetry (and conformation) present in the same crystal.[8]

Chain axes parallelism is mainly related to the need for close packing. In fact, piling up layers made of parallel cilindrical shaped chains, optimum space filling is realized when the ridges of a layer face the grooves of the layers below and above.[11] Packing of the chains, however, is also driven by the need for optimum intermolecular interactions. Some interactions, such as those between planar aromatic cores, are strongly orientation dependent.[12] If the aromatic cores that are present along the chain of a semiflexible polymer have internal conformational flexibility, as often occurs for "mesogenic groups", the needs for chain axes parallelism and optimum intermolecular interactions may easily conform to each other, but if the aromatic cores are conformationally blocked, the two needs may come in contrast and the question arises of which is dominant in the packing.

Naphthalene is a typical conformationally blocked aromatic core. Main chain polymers and copolymers based on various dihydroxynaphthalene isomers, either semiflexible[13,14] and full rigid[15] ones, have been studied in relation to liquid crystal behavior. Some years ago we have reported the crystal structure of a dicarboxylic acid[16] model of simple polyesters based on 2,6-dihydroxynaphthalene and aliphatic dicarboxylic acids.[17] In the present note we report on the crystal structure of two isomeric derivatives of the diacid described in ref 16, based on 1,5- and 2,7-dihydroxynaphthalene: 4,4′-[1,5-naphthylenebis(oxycarbonyl)]dibutyric acid (A15) and 4,4′-[2,7-naphthylenebis(oxycarbonyl)]dibutyric acid (A27).


A15


A27

The different substitution onto the naphthalene ring changes the shape of the molecule and, therefore, the overall shape of the molecular rows formed in the

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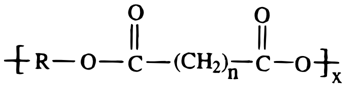
**Table 1. Crystal, Collection, and Refinement Data for A15 and A27**

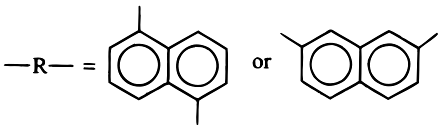
| | A15 | A27 |
|---|---|---|
| chem formula | $C_{20}H_{20}O_8$ | $C_{20}H_{20}O_8$ |
| cryst syst | monoclinic | monoclinic |
| space group | $P2_1/c$ | $P2_1/c$ |
| $a$ (Å) | 16.764(3) | 9.0681(9) |
| $b$ (Å) | 5.401(7) | 6.003(2) |
| $c$ (Å) | 10.342(5) | 34.905(4) |
| $\beta$ (°) | 89.30(3) | 99.686(8) |
| $V$ (Å$^3$) | 936(1) | 1873.0(7) |
| $Z$ | 2 | 4 |
| $d_c$ (g cm$^{-3}$) | 1.375 | 1.377 |
| $\mu$ (mm$^{-1}$) | 0.11 | 0.11 |
| $T$ (K) | 295 | 295 |
| cryst size (mm$^3$) | 0.6 × 0.5 × 0.05 | 0.6 × 0.4 × 0.2 |
| reflns collcd | 2106 | 3314 |
| reflns unique and $R_{int}$ | 1981, 0.0258 | 3263, 0.0409 |
| range of indices | $-21 \le h \le 21$<br>$0 \le k \le 6$<br>$0 \le l \le 12$ | $-10 \le h \le 10$<br>$0 \le k \le 7$<br>$0 \le l \le 41$ |
| $2\theta_{max}$ | 53.40 | 49.84 |
| paramrs refined | 130 | 256 |
| $R_w$ ($F^2$), $S$ (all reflections) | 0.144, 1.089 | 0.210, 0.983 |
| $R(F)$ (reflections with $I > 2\sigma(I)$) | 0.0505 (1285) | 0.0666 (1264) |
| max and min peak in the final difference Fourier map (e Å$^{-3}$) | 0.22, −0.20 | 0.22, −0.17 |
| max shift-to-error ratio in the last refinement cycle | 0.01 | 0.01 |

crystal, and this, in turn, offers the possibility of investigating, in a rather systematic way, the mode of packing of rows having different shapes but identical chemical compositions.

These diacids could be considered as models for the crystal packing of polyesters having formula



$$\left[ R-O-\overset{\displaystyle O}{\overset{\|}{C}}-(CH_2)_n-\overset{\displaystyle O}{\overset{\|}{C}}-O \right]_x$$



However, it should be noted that although the hydrogen bonded rows of the diacids have a close resemblance with the covalently bonded chains of the corresponding polymers, the mechanism of crystallization is presumably quite different in the two cases; therefore the validity of these compounds as models for the crystal structure of polymers has to be taken with some caution.

## Experimental Section

Compounds A15 (mp 466 K) and A27 (mp 419 K) were prepared, in 65% and 60% yields, by reaction of commercial 1,5- and 2,7-dihydroxynaphthalene with glutaric anhydride by following the same procedure reported in ref 16 for the 2,6-dihydroxynaphthalene-based isomer. Single crystals suitable for X-ray diffraction analysis were grown in both cases by slow evaporation from ethanol. Weissenberg and oscillation photographs indicated for both compounds monoclinic system and the $P2_1/c$ space group. Accurate cell parameters were obtained through a least-squares fit to the setting angles of 25 accurately centered, strong reflections, in the range 10.66° $\le \theta \le$ 14.81° for A15 and 9.21° $\le \theta \le$ 11.30° for A27 on an Enraf Nonius MACH3 automated single-crystal diffractometer, using graphite monochromated Mo Kα radiation ($\lambda$ = 0.710 69 Å).

**Table 2. Fractional Atomic Coordinates (×10$^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$ × 10$^3$), with Esd's in Parentheses, for A15**

| | $x$ | $y$ | $z$ | $U_{eq}$[a] |
|---|---|---|---|---|
| O1 | 755(1) | −3712(5) | 704(2) | 83(1) |
| O2 | 211(1) | −7278(5) | 1244(3) | 84(1) |
| O3 | 2870(1) | 21(4) | 3544(2) | 65(1) |
| O4 | 3345(1) | −2281(3) | 5150(2) | 47(1) |
| C1 | 720(2) | −5493(6) | 1412(3) | 54(1) |
| C2 | 1248(2) | −5841(5) | 2545(3) | 53(1) |
| C3 | 1775(1) | −3631(5) | 2802(3) | 45(1) |
| C4 | 2290(1) | −3958(5) | 3979(2) | 43(1) |
| C5 | 2842(1) | −1834(5) | 4169(2) | 40(1) |
| C6 | 3937(1) | −502(5) | 5409(2) | 40(1) |
| C7 | 3777(2) | 1367(5) | 6245(3) | 47(1) |
| C8 | 5615(2) | −3029(5) | 3434(2) | 47(1) |
| C9 | 4873(2) | −2799(5) | 3956(2) | 42(1) |
| C10 | 4696(1) | −853(4) | 4834(2) | 36(1) |

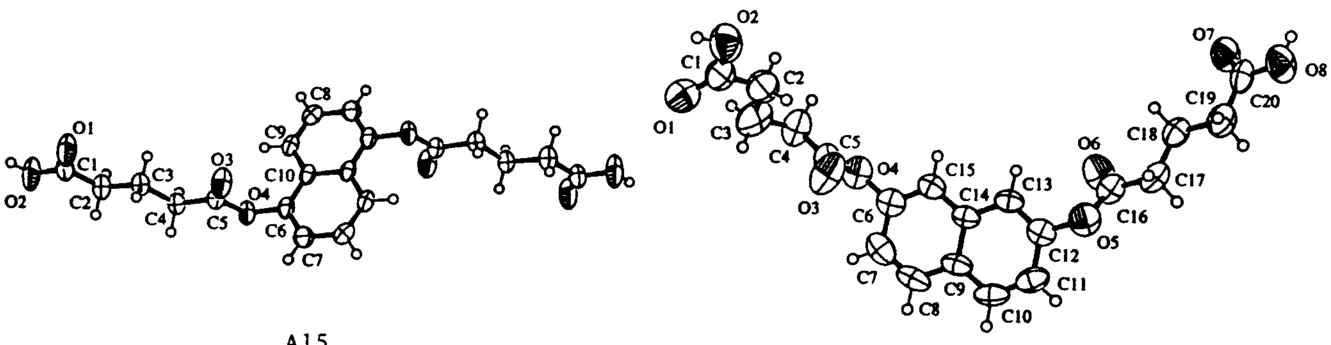
[a] $U_{eq}$ is defined as one-third of the trace of the orthogonalized $\mathbf{U}^{ij}$ tensor.

**Table 3. Fractional Atomic Coordinates (×10$^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$ × 10$^3$), with Esd's in Parentheses, for A27**

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| O1 | 4430(4) | −2772(7) | 223(1) | 90(1) |
| O2 | 5271(5) | −5979(9) | 490(1) | 103(1) |
| O3 | 6272(4) | 274(9) | 1496(1) | 106(2) |
| O4 | 4780(4) | 1423(7) | 1896(1) | 79(1) |
| O5 | 10609(4) | 73(8) | 3581(1) | 86(1) |
| O6 | 8701(4) | −919(8) | 3864(1) | 98(1) |
| O7 | 9544(4) | −7839(7) | 4725(1) | 95(1) |
| O8 | 11831(4) | −8790(9) | 4971(1) | 103(2) |
| C1 | 4747(6) | −4043(14) | 507(2) | 78(2) |
| C2 | 4545(7) | −3247(11) | 908(2) | 92(2) |
| C3 | 3833(6) | −1068(12) | 920(2) | 104(2) |
| C4 | 3639(5) | −352(12) | 1334(2) | 87(2) |
| C5 | 5049(6) | 426(10) | 1568(2) | 69(2) |
| C6 | 6041(5) | 2228(10) | 2161(2) | 63(2) |
| C7 | 6590(7) | 4361(11) | 2092(2) | 77(2) |
| C8 | 7747(7) | 5174(10) | 2349(2) | 74(2) |
| C9 | 8411(6) | 3972(9) | 2678(2) | 58(1) |
| C10 | 9662(6) | 4726(10) | 2941(2) | 70(2) |
| C11 | 10313(6) | 3472(11) | 3236(2) | 70(2) |
| C12 | 9737(6) | 1352(10) | 3293(2) | 62(1) |
| C13 | 8510(5) | 538(9) | 3058(2) | 59(1) |
| C14 | 7824(5) | 1828(8) | 2740(2) | 52(1) |
| C15 | 6614(5) | 1007(9) | 2472(2) | 59(1) |
| C16 | 9999(6) | −1047(10) | 3846(2) | 68(2) |
| C17 | 11122(5) | −2452(9) | 4095(2) | 71(2) |
| C18 | 10424(5) | −4319(9) | 4295(2) | 67(2) |
| C19 | 11553(5) | −5701(10) | 4557(2) | 79(2) |
| C20 | 10867(6) | −7532(10) | 4754(2) | 70(2) |

[a] $U_{eq}$ is defined as one-third of the trace of the orthogonalized $\mathbf{U}^{ij}$ tensor.

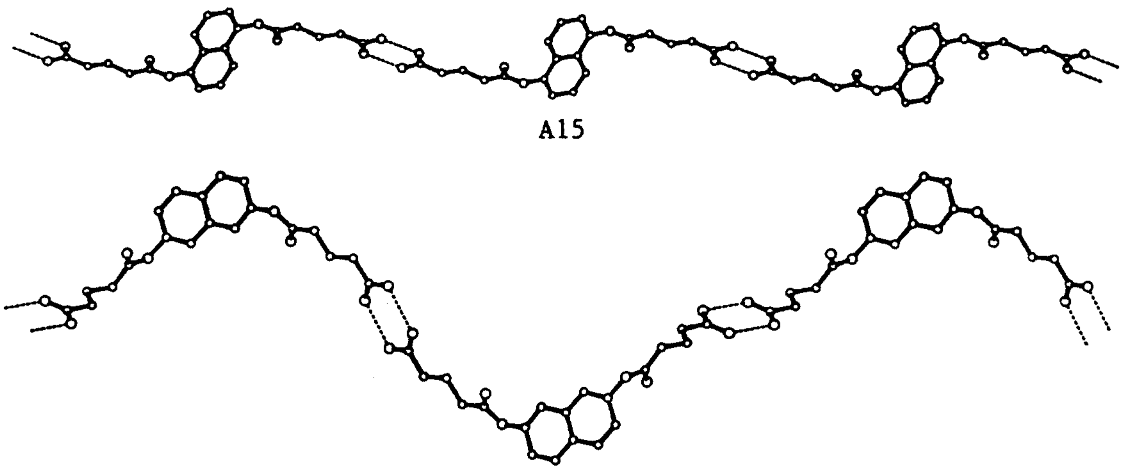
Data collection was performed in the range 1° $\le \theta \le$ 26.8° for A15 and 1° $\le \theta \le$ 25° for A27, in the $\omega/\theta$ scan mode. During data collection, the intensity of a control reflection, periodically measured, showed only random fluctuations. Lorentz and polarization corrections were applied, no correction for absorption and secondary extinction was introduced. Both structures were solved by direct methods (SHELXS program of SHELX-97 package[18]) and refined by the full matrix least-squares method (SHELXL program of the same package). Some crystal, collection, and refinement data are reported in Table 1. C and O atoms were given anisotropic displacement parameters, H atoms were placed in calculated positions and refined by the riding model with $U_{iso}$ equal to $U_{eq}$ of the carrier atom, with the exception of the H atoms of the ordered carboxy groups whose coordinates were refined. Refinement was on $F^2$ against all independent measured reflections; sigma weights were introduced in the last refinement cycles. A conventional $R$ factor on $F$, based on reflections with $I > 2\sigma(I)$, has also been calculated and reported in Table 1.



A15

A27

**Figure 1.** Molecular structures of A15 and A27. Thermal ellipsoids are at the 50% probability level.



A15

A27

**Figure 2.** Molecular rows of A15 and A27.

**Table 4. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for A15 and A27**

| | | |
|---|---|---|
| | A15 | |
| O1−C1 1.210(4) | O2−C1 1.300(4) | C6−C7 1.354(4) |
| C6−C10 1.410(3) | C8−C9 1.356(4) | C9−C10 1.419(4) |
| C10−C10* 1.420(5) | | |
| O1−C1−O2 122.4(3) | O1−C1−C2 123.5(3) | O2−C1−C2 114.1(3) |
| C7−C6−C10 122.6(2) | C6−C10−C9 123.4(2) | |
| O2−C1−C2−C3 −174.1(3) | C4−C5−O4−C6 176.6(2) | C5−O4−C6−C10 −94.4(3) |
| | A27 | |
| O1−C1 1.247(7) | O2−C1 1.261(7) | O7−C20 1.201(6) |
| O8−C20 1.298(6) | C6−C7 1.408(8) | C6−C15 1.342(7) |
| C7−C8 1.352(8) | C8−C9 1.403(7) | C9−C10 1.409(7) |
| C9−C14 1.423(7) | C10−C11 1.330(7) | C11−C12 1.403(8) |
| C12−C13 1.359(7) | C13−C14 1.408(7) | C14−C15 1.406(7) |
| O1−C1−O2 124.3(7) | O1−C1−C2 119.6(7) | O2−C1−C2 116.1(7) |
| O7−C20−O8 121.7(6) | O7−C20−C19 124.4(5) | O8−C20−C19 114.0(5) |
| C2−C3−C4−C5 76.5(7) | C4−C5−O4−C6 178.5(5) | C5−O4−C6−C15 −98.7(6) |
| C11−C12−O5−C16 134.6(5) | C12−O5−C16−C17 174.4(5) | |

## Results and Discussion

Molecular structures of compounds A15 and A27 are reported in Figure 1. Fractional atomic coordinates for the crystallographically independent units are reported in Tables 2 and 3. Selected bond lengths, bond angles and torsion angles are reported in Table 4.

Molecules of A15 lie on crystallographic inversion centers and, therefore, have $C_i$ ($\bar{1}$) point symmetry. In both structures the naphthalene ring is planar and the C−C bonds in the ring are not of equal length, C6−C7 and C8−C9 for A15 and C6−C15, C7−C8, C10−C11, and C12−C13 for A27 being shorter than the others, as expected.[16]

The conformation of the aliphatic chain in A15 is trans planar, while a torsion angle of the gauche type is observed in one aliphatic tail of A27. The values of the torsion angle around the O4−C6 bond for A15 and around O4−C6 and O5−C12 for A27 are typical of ester groups linked to aromatic rings.

Bond lengths in the carboxy group of A15 indicate that no disorder is present,[5] while almost complete disorder is present in one carboxy group of A27.

In both crystal structures each molecule is bonded through a hydrogen bond between the carboxylic groups to two others, so that extended rows are formed, Figure 2; these rows are centrosymmetric since hydrogen bonding occurs across crystallographic inversion centers. Translational repetition along the row is accomplished after one monomeric unit (molecule) for A15 and after two for A27; this is a consequence of carboxy groups

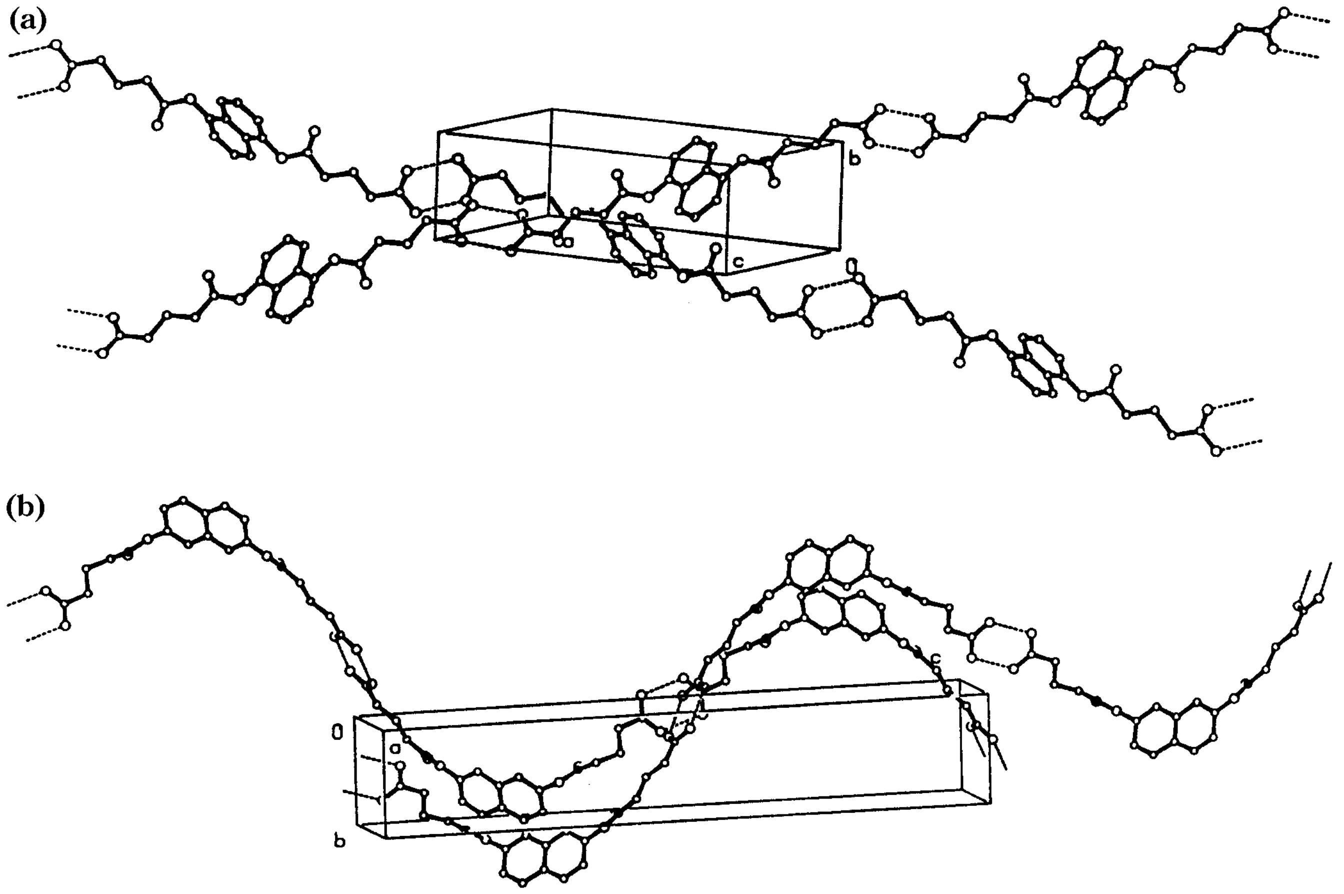


**Figure 3.** Crystal packing of A15 (a) and A27 (b).

**Table 5. Hydrogen Bond Distances and Angles**[a]

| | | |
|---|---|---|
| A15 | O2···O1(i) = 2.656(3) Å | O2−HO2···O1(i) = 174(3)° |
| A27 | O1···O2(ii) = 2.653(6) Å | |
| A27 | O8···O7(iii) = 2.687(6) Å | O8−HO8···O7(iii) = 174(6)° |

[a] (i) = $-x, -1 - y, -z$; (ii) = $1 - x, -1 - y, -z$; (iii) = $2 - x, -2 - y, 1 - z$.

pointing to the same side of the naphthalene ring in A27 and to opposite sides in A15; rows of A27, therefore, have a more wavy shape than for A15. Intermolecular distances between hydrogen bonded O atoms, see Table 5, are in agreement with literature values.[5] The cyclic hydrogen bonded dimers C1, O1, O2, C1(i), O1(i), O2(i) for A15 and C1, O1, O2, C1(ii), O1(ii), O2(ii) and C20, O7, O8, C20(iii), O7(iii), O8(iii) for A27 are planar to within 0.02 Å.

As shown in Figure 3, nonparallel rows of hydrogen bonded molecules run through the crystal. In particular, two nonparallel directions are possible, so that the packing may be considered as a stacking of planes of parallel rows, in which the directions of rows belonging to consecutive planes are not parallel, Figure 4. Nonparallelism of row axes in the present structures arises in a simple way from the class symmetry of space group $P2_1/c$, which is $2/m$. In fact, as far as A15 is concerned, the vector of translational repetition of the row to which the crystallographically independent half-molecule belongs is the $\mathbf{a} + \mathbf{b} + \mathbf{c}$ lattice vector, while it is the $\mathbf{a} - \mathbf{b} + \mathbf{c}$ lattice vector for A27. Since these vectors have a component along **b** (unique axis), rows nonparallel to these directions are generated by operations 2 and $m$ of the point group. The angle between nonparallel rows in the crystal is 30.5° for A15 and 19.7° for A27.

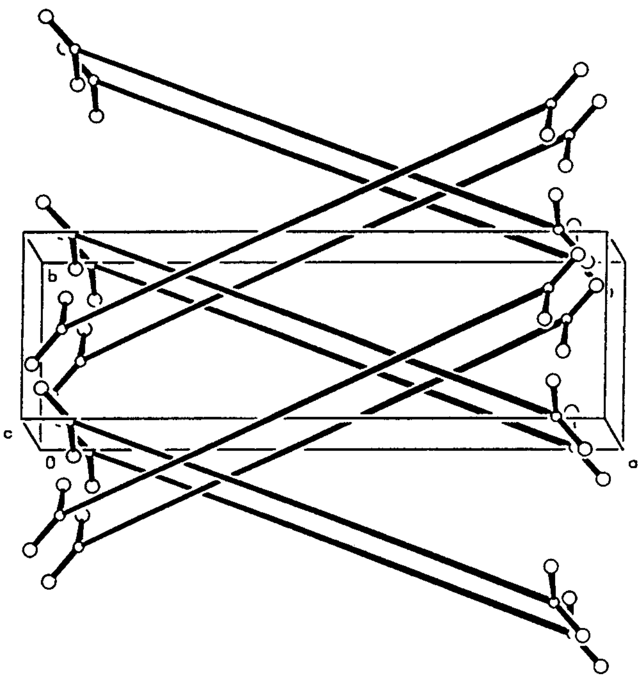


**Figure 4.** Schematic crystal packing of A15. Molecules are represented through a virtual bond between C atoms of the carboxy groups.

Packing of the rows shows in both structures a lateral correspondence between chemically homologous molecular sections (aliphatic−aliphatic, aromatic−aromatic), at variance with the 2,6 isomer,[16] for which an intercalated packing of parallel chains was observed. In particular, Figure 5, the lateral packing of the aromatic

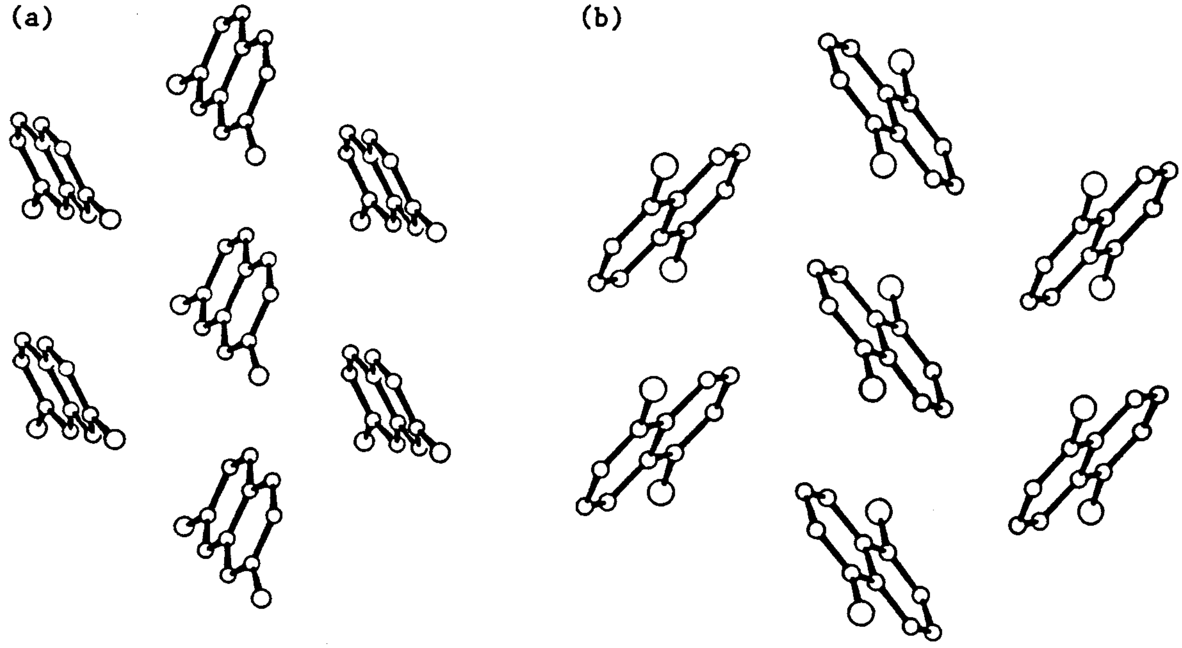


**Figure 5.** Lateral packing around a central naphthalenedioxy ring for A15 (a) and A27 (b). Other atoms are omitted for clarity.

groups shows six nearest neighbors around each central naphthalene ring (herringbone pattern). The relative orientation of these aromatic rings is either of the face to face type (closest contacts of 3.2 Å for A15 and 3.7 Å for A27) or face to edge (closest contacts of 3.7 Å for A15 and 3.5 Å for A27). These intermolecular contacts are rather short and produce a dense packing (the crystal density of A15 is only 0.7% less than that for the 2,6 isomer, for which a parallel arrangement of the rows is present, while that of A27 is 0.6% less) that is very similar to the lateral packing of crystalline naphthalene.[19]

Actually, nonparallelism of row axes in the two structures seems a consequence of the lateral packing of naphthalene groups. In fact, while face to face lateral contacts may always occur among naphthalene groups belonging to rows related by translation or by an inversion center, and therefore being parallel, it is clear from Figure 5 that for the face to edge ones a different orientation of the rows is required.

Face to face and face to edge contacts are typical of the lateral packing of compounds containing medium size aromatic cores,[12,20] and this pattern has been found in several dicarboxylic acids containing mesogenic cores.[7−9] In these cases, however, parallelism of row axes is maintained substantially because these aromatic cores (e.g., *p*,*p*′-bis(acetophenon)azine, *p*,*p*′-biphenyl) have internal conformational freedom allowing also face to edge lateral contacts to be established among centrosymmetrically related, and therefore parallel, rows; this conformational flexibility is obviously absent in the naphthalene group.

Therefore, in chains containing a regular alternance of aliphatic and aromatic sections (main chain semiflexible liquid crystalline polymers belong to this type), the possibility exists that specific and orientation dependent interactions among the aromatic cores, if they are dominant in the packing, lead to alternative structures with nonparallel placement of the chains in the crystal. To this respect, some conformational flexibility of the aromatic core seems a feature that can favor the parrallel packing of chains and it is still the case of noticing that most of the ”good” mesogenic groups actually have internal conformational flexibility.[21]

The crystal structure analysis of dicarboxylic acids based on others dihydroxynaphthalene isomers, as well as the synthesis and structural characterization of the corresponding polymers are under way in our laboratory and will be reported in future publications.

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**Supporting Information Available:** Tables of atomic coordinates, thermal parameters, bond lengths and angles, and torsion angles for A15 and A27 (13 pages). Ordering information is given on any current masthead page.

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