The Melting Point Alternation in α,ω-Alkanedicarboxylic Acids[†]

Venkat R. Thalladi,* Markus Nüsse, and Roland Boese*

Contribution from the Institut für Anorganische Chemie, Universität-GH Essen, Universitätsstrasse 5-7, D-45117 Essen, Germany

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Abstract: Single-crystal X-ray diffraction analyses of α,ω-alkanedicarboxylic acids ($HOOC-(CH_2)_{n-2}-COOH$, $n = 2-10$) have been carried out at 130 and 298 K. Dimorphism is prevalent in odd carbon members, and the crystal structures of α- and β-forms of C7-diacid have been determined. Diacids show an alternation in their melting points with members containing an even number of carbon atoms exhibiting systematically higher melting points compared to odd ones. On the contrary, the solid-state densities of odd members with $C_n \geq 5$ are higher than those of even members. Closest packing is therefore not the reason for alternating melting points in diacids. Diacids with $C_n \geq 5$ show distinct packing regularities within even series and also within α- and β-series of odd members. The gross structural features are similar in even and (both forms of) odd diacids: (a) carboxy groups form hydrogen bonded dimers at both ends of the molecules, leading to infinite chains, and (b) methylene chains stack into columns through hydrophobic interactions. However, there are certain differences within these similar packing patterns that are important in the context of melting point alternation: (a) molecules are offset along their length within the columnar stacks in even members, whereas such an offset is absent in both forms of odd members, and (b) molecules in both modifications of odd members exhibit twisted molecular conformations with severe torsions as opposed to the non-twisted all-*trans* conformation in the even members. Energies of the ideal and observed conformations have been computed with the hybrid-DFT method B3LYP and 6-31G* basis set. A simple geometrical model has been developed wherein the even and odd members are described as modified parallelograms and trapezoids, respectively. It is shown that, whereas the packing of parallelograms allows an offset which reduces the repulsions between the carboxy dimers of adjacent hydrogen bonded chains, a similar offset is forbidden for the packing of trapezoids. The model also suggests the reason for the prevalence of dimorphism in odd diacids. Because the twisted molecular conformations in odd diacids are associated with high energy, they have lower melting points. The melting point alternation in diacids is therefore attributed to the geometry-allowed or -forbidden attainment of an offset packing with a non-twist molecular conformation.

Introduction: An Odyssey through 120 Years of Research

The earliest work related to the phenomenon of melting point alternation was published in 1877 which dealt with α,ω-alkanedicarboxylic acids (diacids hereafter) and fatty acids.[1] In this very early article, Baeyer prophetically stated that “a law which would tell that in a homologous series a compound with odd number of carbon atoms has a relatively lower melting point than those with an even number would have considerable interest in molecular physics and ask for investigations if the crystal form, solubility etc., are correlated with the number of carbon atoms.” Since then the alternation phenomenon is also identified in *n*-alkanes and many of the end-substituted *n*-alkanes.[2] The melting point is not the only property that exhibits an alternating trend. Other solid-state properties such as solubility and sublimation enthalpy also display pronounced alternation. The properties related to the liquid state, however, do not show any alternating trend. In this article diacids with an even or odd number of carbon atoms are referred to as even or odd members, respectively.

Although the alternation phenomenon is recognized in a wide range of *n*-alkane derivatives, solid-state structural studies on these compounds have been hampered by the fact that many of these compounds are liquids or semisolids at ambient temperature. Diacids on the other hand are different. Even the lowest member of the series, C2-diacid,[3] is a solid (mp 189.5 °C) with remarkable crystallinity. For this reason, diacids have been the subject of crystallographic investigations, unlike many other *n*-alkane derivatives, since the turn of the twentieth century. Much work has been published, and in the following we refer to some important contributions which lay background for the present work.

The first comprehensive crystallographic work on diacids has been carried out by Caspari in 1928 who determined the unit cell dimensions of C6- to C10- and C13- and C18-diacids by means of X-ray photographs.[4] He observed that the crystals fall into two groups, according to odd or even number of carbon atoms in the molecule with same cell breadth and depth for all, and that the long axis corresponds to the chain length. From this study he reasoned that “the difference in crystal structure cannot be unconnected with the well-known alternation in their

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[†] *The Melting Point Alternation in n-Alkanes and Derivatives*, Part 4. For parts 1, 2, and 3, see: refs 14, 15, and 16, respectively.

(1) Baeyer, A. *Ber. Chem. Ges.* **1877**, *10*, 1286.

(2) Substantial information on melting and boiling points, solubilities, refractive indices and sublimation enthalpies can be found in: Breusch, F. L. *Fortschr. Chem. Forsch.* **1969**, *12*, 119.

(3) Diacids are well-known after their common names viz. oxalic (C2), malonic (C3), succinic (C4), glutaric (C5), adipic (C6), pimelic (C7), suberic (C8), azelaic (C9). and sebacic (C10). For ease of notation we refer to any diacid by the total number of carbon atoms it contains. Thus, for example, C6-diacid refers to adipic acid.

(4) Caspari, W. A. *J. Chem. Soc.* **1928**, 3235.

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melting points." It is interesting to note that the melting point alternation in diacids is "well-known" in 1928, although the reason for its existence is still waiting to be uncovered.

Polymorphism has been identified in the lower analogues of diacids and also in the odd members. During the years 1930–1935 Dupré la Tour studied the phase transitions in odd diacids in the range C3–C17 and also in C4-diacid.[5] His work established that dimorphism is a common phenomenon among odd diacids. He has determined the unit cell dimensions for both modifications of each studied member up to C9-diacid. Polymorphism is a disturbing problem for any study that relates crystal structure of a compound to its properties. The polymorphic behavior of diacids questions the explanations offered to their melting point alternation.

The first attempts to relate crystal structures of diacids and their melting point alternation appeared around 1940 from the research of two distinguished laboratories. MacGillavry and co-workers studied the structures of stable forms of C4-, C5-, C6-, and C7-diacids during the years 1939–1948.[6] Around the same time Robertson and co-workers studied the structures of stable forms of C4-, C5-, C6-, and C10-diacids.[7] Both the groups worked with two-dimensional X-ray techniques (photo or film data) and determined the positional parameters of non-hydrogen atoms using two-dimensional least-squares analyses. From such primitive data these authors deduced the following differences between even and odd diacids and ascribed these differences as possible reasons for the melting point alternation. (a) Alternating, long and short, C–C bonds are present along the carbon chain in the even members, whereas the distribution of C–C bond lengths is normal in the odd members. (b) Short intermolecular C···O approaches in the range 3.2–3.3 Å seen in the even members are absent in the odd members. With regard to these short C···O distances in the even members Robertson and co-workers[7b] state that "the order of this approach distance would appear to indicate some very weak and unusual type of hydrogen bridge involving a carbon atom." The authors were referring to what is today known as C–H···O hydrogen bond.[8] (c) Odd diacids possess a twisted molecular conformation in the crystal structure as opposed to the extended conformation seen in even diacids.[9]

There are several limitations to these observations and their consequent implications. These observations were made on a limited number of structures (C8- and C9-diacids not studied). The structures were not accurately determined. It is not clear if one or more of these factors (or some other factor which could not be identified from these data) is responsible for the alternating melting points. Even if one or more of these factors is responsible for the melting point alternation, the answer to the most critical question—why a particular factor is seen in the even members and not in the odd members, or vice versa?—has not been identified. Further, polymorphism which is very common in the odd members[5] has not been considered because of the lack of structural data. The present study aims to overcome these problems and provides a logical explanation for the existence of melting point alternation in diacids.

Extensive investigations on diacids have been performed by Housty and co-workers during the years 1964–1968 who determined the crystal structures of C6-, α-C7-, C8-, α- and β-C9-, C10-, α-C11-, C12- and α-C13-diacids.[10] They collected the data on films and estimated the intensities visually. However, their refinements included three-dimensional least-squares analyses. Although their studies are comprehensive, they are restricted to individual crystal structure determinations and to some comparisons within even or odd series. Correlations between the even and odd structures with their alternating physical properties have not been attempted by these authors.

In the intervening years of above notable studies (between 1877 and 1968)[11] and in the hiatus that followed,[12] diacids have been the subject of several investigations which include: (a) some independent single crystal X-ray and neutron structure determinations, (b) powder X-ray diffraction, (c) phase-transition experiments using DSC (differential scanning calorimetry) and DTA (differential thermal analysis), (d) spectroscopic measurements (IR and Raman), and (e) solid-solution studies. The fact that none of these studies dealt with the melting point alternation clearly indicates the complexity of the problem.

When we began our work on diacids, each member of the series (up to C10) had been crystallographically studied at least twice. However, the available data is very primitive in most cases. Some details of the best determination among the

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Table 1. Crystallographic Information Available for a Given Diacid[a]

C$_n$[b]	method[c]	data available[d]	T (K)[e]	year [ref]
2 (α-form)	3d X-ray	C	300	1974 [12a]
2 (β-form)	3d X-ray	C	300	1974 [12a]
3 (α-form)	3d X-ray	C	300	1994 [12k]
3 (β-form)	2d X-ray	A	300	1931 [5b]
4 (α-form)	2d X-ray	B	300	1944 [11e]
4 (β-form)	3d neutron	C	77	1981 [12e]
5 (α-form)	2d X-ray	A	300	1932 [5c]
5 (β-form)	2d X-ray	B	300	1949 [7d]
6	2d X-ray	C	300	1965 [10e]
7 (α-form)	2d X-ray	C	300	1966 [10h]
7 (β-form)	2d X-ray	B	300	1948 [6d]
8	3d neutron	C	18.4	1994 [12l]
9 (α-form)	2d X-ray	C	300	1967 [10k]
9 (β-form)	2d X-ray	C	300	1967 [10k]
10	2d X-ray	C	300	1966 [10 g]
11 (α-form)	2d X-ray	C	300	1966 [10j]
12	3d X-ray	C	300	1982 [12f]
13 (α-form)	2d X-ray	C	300	1968 [12l]
16	2d X-ray	A	300	1928 [4]

[a] All determinations performed on single crystals. [b] Number of C-atoms in the molecule. [c] 2d X-ray refers to the data collected with photo (Weissenberg or oscillating) or film techniques with visual estimation of intensities. 3d X-ray and 3d neutron refer to the data collected with an automated diffractometer. [d] A = unit-cell parameters only; B = coordinates of non-H-atoms only; C = coordinates of all atoms. [e] Temperature of the data collection. 300 K refers to room-temperature data.

presently known structures of each diacid are recorded in Table 1. It may be seen that most of the data is based on photographic/film techniques. Such data are not accurate enough to use them at a fine detail to identify the differences between the crystal packing of even and odd members. In two important cases (β-forms of C5- and C7-diacids)[13] the H-atom positions are not determined. In light of these structural and interpretational shortcomings and ambiguities, and especially in light of our continuous interest in the exploration of structure−property relationships in the series of *n*-alkanes and their derivatives,[14−16] we have undertaken single-crystal X-ray analyses of diacids from C2 to C10 at 130 K. Because polymorphism is dominant in odd diacids, α- and β-forms of C7-diacid have been studied. The crystals of the α-form could not be cooled to 130 K without destruction (presumably because of the transition to the ordered phase), and the X-ray data for this form has been collected at 298 K. For comparison purposes the data for all other crystals have also been collected at 298 K. Here we present our results based on these two data sets. Not only do these data provide accurate and reliable details of individual structures, but they also permit a validity check to see if the overall trend in structural properties remained the same or changed with the temperature.[17]

Experimental Section

X-ray Crystallography. Commercially available diacids (C2 −C10 from Fluka) were used for crystallization as received. In most cases slow cooling of saturated methanol solutions gave single crystals suitable for X-ray diffraction analysis. Crystallization of C2-diacid from methanol or acetone resulted in the diester or dihydrate, respectively. Morphologically distinguishable α- and β-forms of C2-diacid were obtained in the same flask by slow cooling of saturated ether solutions under nitrogen atmosphere. The X-ray data for the stable form (α-form) were collected. Crystals from the commercial sample of C7-diacid were found to belong to the stable β-modification. When a methanol solution of C7-diacid was slowly cooled the crystals of metastable α-form were obtained. The X-ray data for this modification were collected at 298 K. For all other structures reported in this work the data were collected at 130 and 298 K on a Bruker SMART area detector diffractometer using Mo Kα radiation. The structure solutions and refinements were carried out using SHELXS/L programs built-in with the SHELXTL-5.03 suite. All non-H-atoms were refined anisotropically. Hydroxy H-atoms were located from a difference Fourier map and refined isotropically without constraints. Methylene H-atoms could be located from difference Fourier maps in many cases (especially at 130 K), but for consistency they are generated using geometrical routines in SHELXL program and refined using riding model. Only the H-atoms of the central methylene groups (located on the special positions) in odd diacids were taken from a difference Fourier map and refined isotropically without constraints. Salient details of crystallographic information for the data at 130 K are given in Table 2. Only the cell information is given for the data at 298 K in Table 3. Further details of X-ray diffraction analyses are given in Supporting Information.

Differential Scanning Calorimetry. DSC experiments on C2- to C10-diacids were carried out with a Du Pont 910 differential scanning calorimeter and their melting points were recorded (Table 2). We note that these diacids melt in a narrow range. In all the odd cases, and in the case of C2- and C8-diacids, enantiotropic phase transitions were observed. The phase transitions in C2-diacid and in odd diacids correspond to α- and β-modifications. Attempts to grow the single crystals of the metastable phase of C8-diacid were not successful.

Energy Calculations. The Gaussian-98 program[18] was used for the hybrid density functional theory (DFT)[19] calculations on C5- to C10-diacids. Molecular geometries were taken from the crystal structures and optimized without any constraints using the method B3LYP[20] with the 6-31G* basis set.[21] In all of the cases energy minimization led to a structure which was very close to an all-*trans* conformation. Experimentally observed torsion angles were incorporated into these geometry optimized structures and their single point energies were computed at the same level.

Results and Discussion

Some Previous Misconceptions Resolved. Before we get into the fine details of the crystal packing of diacids, it is

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[13] Some confusion exists in the nomenclature of α- and β-forms of odd diacids with $C_n \geq 5$. We adopt the naming from the Housty and co-workers (ref 10k): β is the stable form at room temperature in which the molecular symmetry retained (space group $C2/c$, $Z = 4$), and α is the metastable form in which the molecular symmetry is lost (space group $P2_1/c$, $Z = 4$). Dupré la Tour (ref 5) showed that in odd diacids stable to metastable phase transition takes place before melting.

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[17] These data are also useful for those who are dealing with solid-state properties at variable temperatures. For example, van der Waals radii of many atoms have been found to vary with temperature: Kirchner, M. T.; Boese, R., unpublished results.

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Table 2. Crystallographic Data for Diacids at 130 K[a]

C_n[b]	2 (α-form)	3 (β-form)	4 (β-form)	5 (β-form)[c]	6	7 (β-form)	8	9 (β-form)	10
emp. form.	$C_2H_2O_4$	$C_3H_4O_4$	$C_4H_6O_4$	$C_5H_8O_4$	$C_6H_{10}O_4$	$C_7H_{12}O_4$	$C_8H_{14}O_4$	$C_9H_{16}O_4$	$C_{10}H_{18}O_4$
form. wt.	90.04	104.06	118.08	132.12	146.14	160.16	174.20	188.22	202.24
mp (°C)	189.5	135.6	188	99	153	106	144	106.5	134.5
cryst. syst.	orthorhombic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	*Pbca*	$P\bar{1}$	$P2_1/c$	$C2/c$	$P2_1/c$	$C2/c$	$P2_1/c$	$C2/c$	$P2_1/c$
a (Å)	6.4298(1)	5.1604(6)	5.4769(4)	12.9769(6)	7.1870(14)	17.7028(9)	8.7912(7)	22.6366(1)	10.9106(4)
b (Å)	6.0600(2)	5.3319(5)	8.7817(7)	4.7484(2)	5.1626(11)	4.7270(2)	5.0681(4)	4.7143(1)	5.0109(2)
c (Å)	7.8030(3)	8.1838(9)	5.0280(3)	9.6955(4)	10.015(2)	9.6713(4)	9.8995(8)	9.6162(3)	9.7936(1)
α (deg)	90	108.083(2)	90	90	90	90	90	90	90
β (deg)	90	101.280(2)	92.928(2)	98.304(2)	110.856(6)	106.580(1)	96.083(2)	110.809(2)	93.451(3)
γ (deg)	90	95.230(2)	90	90	90	90	90	90	90
Z	4	2	2	4	2	4	2	4	2
V (Å^3)	307.02(2)	207.11(4)	242.51(3)	591.17(4)	347.25(12)	775.66(6)	438.59(6)	959.26(4)	534.46(3)
D_{calc} (mg/m^3)	1.948	1.669	1.624	1.484	1.398	1.372	1.319	1.303	1.257
F (000)	184	108	124	280	156	344	188	408	220
2θ range	10.46−56.66	5.38−56.62	7.46−56.76	6.34−56.54	6.06−56.52	4.80−56.42	4.66−56.46	3.84−56.54	3.74−56.76
index ranges	$-3 \le h \le 8$	$-4 \le h \le 6$	$-6 \le h \le 6$	$-14 \le h \le 15$	$-6 \le h \le 5$	$-23 \le h \le 10$	$-10 \le h \le 9$	$-23 \le h \le 28$	$-13 \le h \le 11$
	$-3 \le k \le 8$	$-2 \le k \le 6$	$-10 \le k \le 10$	$-6 \le k \le 2$	$-6 \le k \le 4$	$-4 \le k \le 6$	$-6 \le k \le 1$	$-4 \le k \le 5$	$-5 \le k \le 5$
	$-10 \le l \le 7$	$-8 \le l \le 10$	$-6 \le l \le 1$	$-12 \le l \le 5$	$-4 \le l \le 13$	$-4 \le l \le 12$	$-9 \le l \le 12$	$-12 \le l \le 3$	$-3 \le l \le 12$
R_1	0.042	0.076	0.049	0.046	0.068	0.051	0.053	0.045	0.055
wR_2	0.105	0.186	0.130	0.116	0.193	0.121	0.123	0.108	0.132
GOF	1.193	1.005	1.139	0.990	1.133	0.979	1.068	0.997	0.968
N-total[d]	2228	1736	1984	2308	564	3086	3576	3783	4326
N-indep.[e]	378	745	455	678	444	803	925	979	1022
N-obsd.[f]	336	547	409	518	326	595	696	690	699
variables	32	72	41	50	50	59	59	68	68
C_k*[g]	0.802	0.749	0.777	0.741	0.726	0.727	0.714	0.720	0.704

[a] All the data given in this table belong to the stable forms. [b] Number of C-atoms in the molecule. [c] Termed β, based on the similarity to the β-forms of C7- and C9-diacids. The structure of α-form is unknown. [d−e] Number of collected and independent reflections. [f] Number of observed reflections based on the criteria $I > 2\sigma_I$. [g] Packing coefficient.

Table 3. Crystallographic Data for Diacids at 298 K

C_n[a]	2 (α-form)	3 (β-form)	4 (β-form)	5 (β-form)[b]	6	7 (α-form)	7 (β-form)	8	9 (α-form)[c]	9 (β-form)	10
cryst. syst.	orthorhombic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	*Pbca*	$P\bar{1}$	$P2_1/c$	$C2/c$	$P2_1/c$	$P2_1/c$	$C2/c$	$P2_1/c$	$P2_1/c$	$C2/c$	$P2_1/c$
a (Å)	6.5594(5)	5.1626(6)	5.5261(4)	12.968(3)	7.3712(2)	5.6482(4)	17.6631(11)	8.980(4)	5.67	22.593(2)	10.9936(10)
b (Å)	6.0940(5)	5.3452(6)	8.8807(76)	4.8296(12)	5.1540(2)	9.6538(6)	4.7890(3)	5.0630(14)	9.61	4.7804(5)	4.9858(5)
c (Å)	7.8524(6)	8.4162(12)	5.1051(4)	9.982(2)	10.1449(4)	16.0217(11)	9.8882(7)	10.106(3)	27.39	9.8445(10)	10.1403(10)
α (deg)	90	108.516(2)	90	90	90	90	90	90	90	90	90
β (deg)	90	101.603(2)	91.490(2)	96.872(6)	112.360(2)	108.018(1)	105.612(2)	98.18(4)	136.83	109.934(2)	90.834(2)
γ (deg)	90	95.954(1)	90	90	90	90	90	90	90	90	90
Z	4	2	2	4	2	4	4	2	4	4	2
V (Å^3)	313.88(4)	213.84(5)	250.45(3)	620.7(3)	356.44(2)	830.77(10)	805.57(9)	454.8(3)	1021.1	999.5(2)	555.75(9)
D_{calc} (mg/m^3)	1.905	1.616	1.566	1.414	1.362	1.281	1.321	1.272	1.224	1.251	1.209
C_k*[d]	0.791	0.725	0.745	0.704	0.696	0.673	0.693	0.682	0.654	0.687	0.669

[a] Number of C-atoms in the molecule. [b] Termed β, based on the similarity to the β-forms of C7- and C9-diacids. The structure of α-form is unknown. [c] Data taken from ref 10k. The apparent differences in cell parameters of the α-forms of C7- and C9-diacids arise because of different cell choices. The reduced cell parameters for these two forms (α-C7: $a = 5.648$ Å, $b = 9.654$ Å, $c = 15.252$ Å, $\beta = 92.60°$; α-C9: $a = 5.67$ Å, $b = 9.61$ Å, $c = 18.93$ Å, $\beta = 98.21°$) clearly indicate the systematic gradation in the series. [d] Packing coefficient.

important to resolve some of the earlier misconceptions. Robertson and co-workers[7] emphasize that the alternating bond lengths along the carbon chain in the even members are connected with the melting point alternation. From the present data we find that the C−C bond lengths along the chain in even diacids are randomly distributed. Terminal C−C bond lengths are necessarily shorter because of the sp^2-hybridization of carboxy C-atom. The pattern of bond lengths in C6-, C8-, and C10-diacids is not similar (see Supporting Information). Therefore, the phenomenon of alternating bond lengths in the even members as a reason for their higher melting points can be ruled out.

Another assumption made by Robertson and co-workers[7d] is that the short C···O approaches seen in the even diacids represent non-classical hydrogen bridges and account for the higher melting points of even members. From the present data we find that the C−H vectors of the corresponding methylene groups are not projected in the direction of O-atoms (associated C−H···O angles are around 110° in all even diacids) and therefore these are not C−H···O hydrogen bonds.[22] In fact, these short approaches arise due to the intermolecular electrostatic attractions between carboxy C-atoms (with a partial positive charge) and O-atoms (with a partial negative charge). These contact distances are almost similar in even and odd members[23] and contribute to their stability to a similar extent. The earlier workers have not considered short intermolecular C···O separations arising from carboxy C-atoms because of the inaccuracies in identifying the exact positions of these atoms with two-dimensional X-ray data collection methods. Thus, the fact that short C···O approaches exist only in the even members is not a valid reason to explain their higher melting points.

Inverse Correlation between Melting Points and Densities. An important reason for determining the crystal structures of

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[22] This is also conformed by the accurate H-atom positions obtained from the neutron diffraction data from the C8-diacid made at three different temperatures (ref 12l).

[23] The closest C···O distances at 130 K in Å units are as follows: C4 (3.277), C5 (3.274), C6 (3.159), β-C7 (3.194), C8 (3.116), β-C9 (3.169), and C10 (3.086).

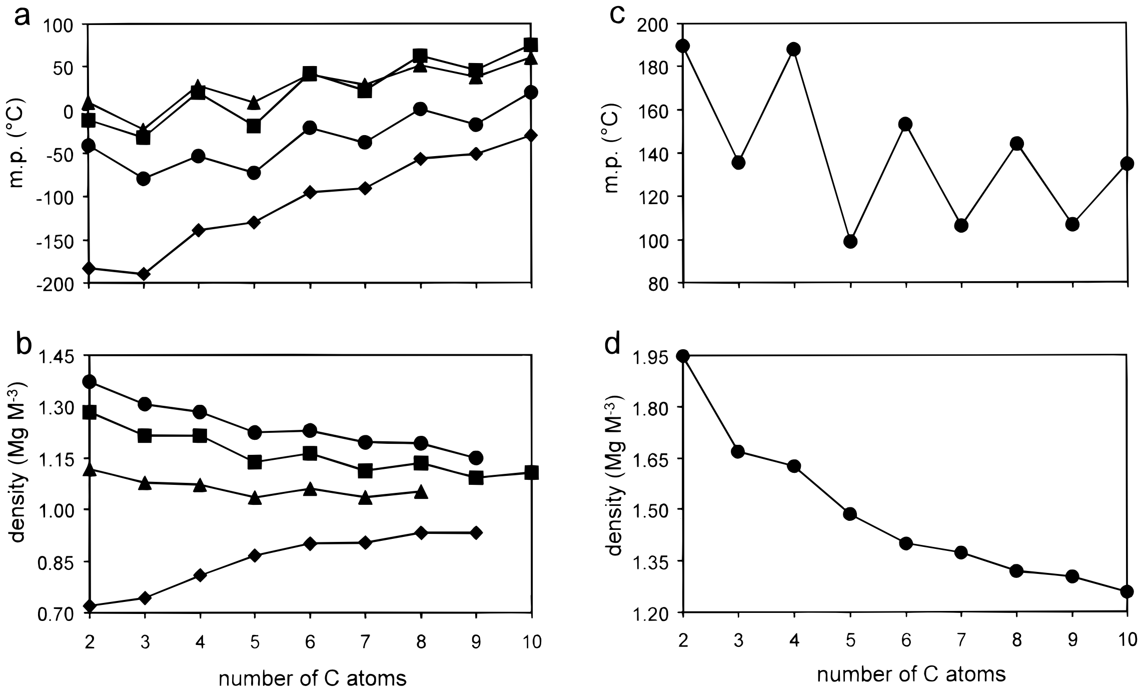

Figure 1. (a) The melting point and (b) density alternation in *n*-alkanes (◆), dithiols (●), diols (■), and diamines (▲). Note that even members possess higher melting points and densities compared to the corresponding odd members. (c) The melting point and (d) density alternation in diacids. Note in (d) that the densities of odd diacids with $C_n \geq 5$ are higher than the corresponding even ones. Notice the similarity between (a) and (c) and the contrast between (b) and (d).

diacids at the same temperature is to compare calculated densities of even and odd members. Our work on *n*-alkanes,[14] α,*ω*-alkanedithiols (dithiols),[16] α,*ω*-alkanediols (diols)[15] and α,*ω*-alkanediamines (diamines)[15] showed that the trend of melting points (Figure 1a) in these four series correlate well with the trend of their solid-state densities (Figure 1b). Even members possess relatively higher melting points and densities than the corresponding odd members. Because many of the structural features of even and odd members are similar in these four series the task had been to find the reasons that favor, and obstruct, the dense packing in even, and odd members, respectively. The implicit assumption in correlating densities and melting points is that melting is primarily controlled by enthalpy when most of the packing features are similar.

In Figure 1c, the melting points of diacids obtained from DSC are plotted against the number of C-atoms in a molecule. We note that different polymorphic phases of a diacid have practically the same melting point. The melting points of even members are distinctly higher than those of odd members. A similar plot for calculated densities at 130 K is displayed in Figure 1d.[24] Surprisingly, the densities of odd members from C5-diacid onward are relatively higher than those of even ones. This is contrary to the density trends in *n*-alkanes, dithiols, diols, and diamines (Figure 1b). Also surprising is the fact that this inverse correlation between densities and melting points of diacids has not been identified during more than 120 years of research on these compounds. This striking fact calls for a rigorous, in-depth structural analysis of diacids and indicates that a factor other than closest packing *is* the reason for melting point alternation in diacids.

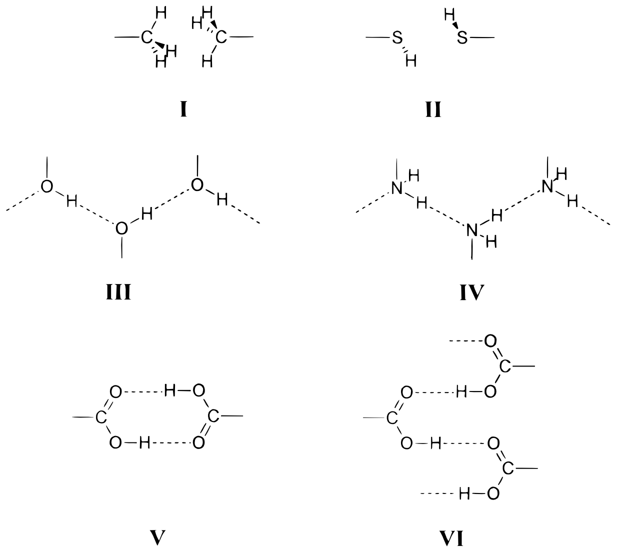

Figure 2. Self-recognition supramolecular synthons of methyl (**I**), thiol (**II**), hydroxy (**III**), amino (**IV**), and carboxy (**V** and **VI**) groups. Note that while each participating group is linked to one other in synthons **I**, **II**, and **V**, they are linked to two others in synthons **III**, **IV**, and **VI**.

Self-Association of End Groups and Methylene Chains. A significant feature in *n*-alkanes, dithiols, diols, and diamines is that the end groups and methylene chains associate with themselves.[14−16] Further, end group−end group and chain−chain interactions occur in separate domains, that is, the two important sets of interactions that are possible in these series are structurally insulated from one another. In *n*-alkanes and dithiols,[14,16] each end group (CH_3 or SH) is connected to one other end group through the supramolecular synthons[25] **I** and **II** (Figure 2). In diols and diamines the hydrogen bonding necessities of OH and NH_2 groups require each of these groups to be connected to two other end groups.[15] The synthons **III** and **IV** thus formed are shown in Figure 2. In diacids too, as will be shown, the end groups (carboxy groups) and methylene chains pack in distinct domains, and we rationalize the important

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(24) The density trend is similar for the data at 298 K too; see Supporting Information.

(25) Desiraju, G. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2311.

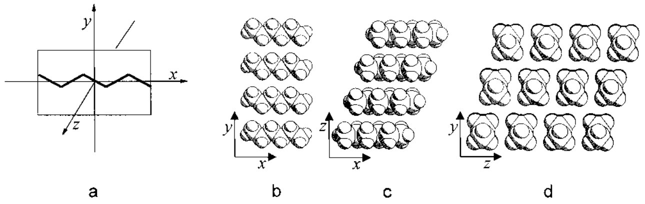

Figure 3. Main chain packing in *n*-hexane. (a) A schematic representation for the packing in three-dimensions. Note that *x, y,* and *z* are not crystallographic axes. The chain axis, *x* passes through midpoints of all the C−C bonds. (b) Intergrooving pattern of methylene groups along *y*. Successive molecules are displaced down the plane (see d). (c) Packing perpendicular to the molecular plane (along *z*) illustrating a different packing pattern of hydrocarbon chains (projection-hollow fitting). (d) View down the chain axis to show packing along *y* and *z* axes. For clarity, all of the molecules are projected onto the plane of the paper.

packing features of these two sets of functionalities independently and then invoke the mutual interplay between the two kinds of interactions.

Carboxy groups are well-known to self-associate in two distinct packing modes **V** and **VI** (Figure 2).[26] A convergent approach of the two carboxy groups links them across an inversion center through two O−H···O═C hydrogen bonds and leads to formation of cyclic dimer **V**. An equally known but less frequent self-association synthon is the catemer **VI** formed from a divergent approach of the carboxy groups. The dimer **V** is the most commonly observed synthon and is also found in the diacids (except in the α-form of C2-diacid which constitutes the catemer **VI**). An important point of relevance is that synthon **V** links a carboxy group to one other, whereas each carboxy group is linked to two others through synthon **VI**. That diacids self-assemble through synthon **V** indicates that they resemble *n*-alkanes and dithiols in terms of one-to-one end group connectivity, and diols and diamines in terms of an interplay between hydrogen bonding and hydrophobic interactions. We take the advantage of these two factors in explaining the melting point alternation in diacids.

A knowledge of the hydrophobic packing in *n*-alkanes is helpful in understanding interchain arrangements in diacids. Molecular packing along their lengths is similar in even and odd members of *n*-alkanes and is illustrated in Figure 3 with the structure of *n*-hexane.[14] An orthogonal notation (Figure 3a) is considered for convenience. The packing perpendicular (along *y* and *z*) to the chain axis (*x*) is of interest in the present context. The molecule in an all-*trans* conformation lies in *xy*-plane. Methylene groups of successive molecules intergroove along *y* at a distance of 4.7 Å and produce a columnar structure (Figure 3b). These columns stack over one another perpendicular to the molecular plane (Figure 3c). The molecules slide along the chain axis (*x*) such that the projections fit into hollows. Typically two kinds of patterns are observed (Figure 3b and c). The significance of these patterns will become apparent in understanding the packing of methylene chains in diacids.

Onset of Packing Regularities from C5-Diacid. Diacids with $C_n \geq 5$ crystallize in the space groups $P2_1/c$ for even members and $C2/c$ for β-forms of odd members with systematic gradations in their unit cell dimensions (Table 2). This suggests two distinctive features: (a) the packing within even series is similar, as also within β-series of odd members, and (b) even and odd (β-form) structures fall into two distinct packing patterns. Molecular symmetry is extended to crystal symmetry in both these cases. The α-modifications of odd diacids crystallize in the space group $P2_1/c$ (Table 3) with a loss of molecular symmetry in the crystal. However, the systematic gradation of the unit cell parameters is still maintained, indicating similar packing within α-series of the odd members.

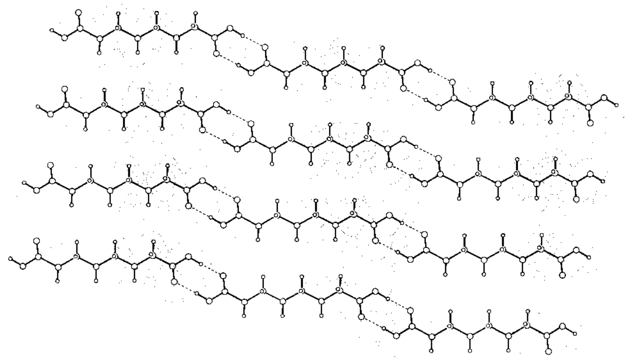

Figure 4. Layer structure in C8-diacid. Molecules lie on inversion centers with an all-*trans* conformation. Lateral molecules are linked through carboxy dimers to form infinite hydrogen bonded chains. Hydrophobic interactions maintain the interchain assembly. Note that the chains are rotated with respect to mean plane of the layer. Contrast the packing of methylene chains in the vertical direction with that in Figure 3b and notice the offset.

The lower members of diacids with $C_n \leq 4$ are polymorphic and do not follow the trend of their higher analogues. In this work, the crystal structures of these members have been determined at the same temperatures and to a similar (high) accuracy for overall comparison purposes. C2-Diacid crystallizes in orthorhombic α- and monoclinic β-modifications. We note that these two are concomitant polymorphs.[27] The α-form of C2-diacid consists of layers of molecules interlinked through catemeric synthons. In the metastable β-form of C2-diacid, and in the stable forms of C3- and C4-diacids molecules are linked through dimer synthon **V** and extend to infinite hydrogen bonded chains. Although the higher analogues constitute similar infinite chain patterns, their interchain packing is different from that of the lower members. The structure of the metastable α-form of C4-diacid is said to be closely related (but not similar) to that of C6-diacid.[11e] However, in the absence of suitable data for this form, and in terms of stable modifications, the packing regularities may be said to begin from the C5-diacid. The following discussion therefore refers to diacids with $C_n \geq 5$.

Even Members. Even diacids with $C_n \geq 6$ have similar crystal structures (Table 2). The crystal structure of C8-diacid is displayed in Figure 4 as a representative example of an even diacid. Molecules lie on inversion centers with fully extended all-*trans* conformation. Carboxy dimer synthons **V** link lateral molecules in an end-to-end manner to generate infinite hydrogen bonded chains. Adjacent chains aggregate into layers through hydrophobic interactions between methylene groups. It is of note that the interchain packing is slightly different from the ideal packing seen in *n*-alkanes (Figure 3b). In even diacids, the molecules are tilted with respect to the layer plane (angle between the mean planes of carbon chain and the layer is ~43°) with a longer interchain separation (5.1 Å) compared to that seen in *n*-alkanes (4.7 Å). Another distinct feature of the interchain packing in even diacids is that the molecules are offset along the length of the chain axis. The contrast between the offset chain packing of an even diacid (Figure 4) and the non-offset situation in *n*-alkanes (Figure 3b) may be noted. The

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(26) Leiserowitz, L. *Acta Crystallogr.* **1976**, *B32*, 775.

(27) Concomitant polymorphism is also reported for C9-diacid (ref 11c). For a review on this phenomenon, see: Bernstein, J.; Davey, R. J.; Henck, J.-O. *Angew. Chem., Int. Ed.* **1999**, *38*, 3440.

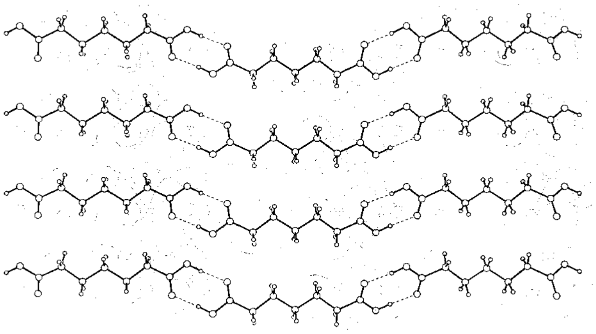

Figure 5. Layer structure in the *β*-form of C7-diacid. Molecules lie on 2-fold axes with a twisted conformation. Lateral molecules are linked through carboxy dimers to form infinite hydrogen bonded chains. Hydrophobic interactions maintain the interchain assembly. Notice the similarity between methylene chain packing with that in Figure 3b and the absence of offset (contrast with Figure 4). Note that while alternating carboxy dimers along the chain are in inclined planes, they are present in parallel planes down the column.

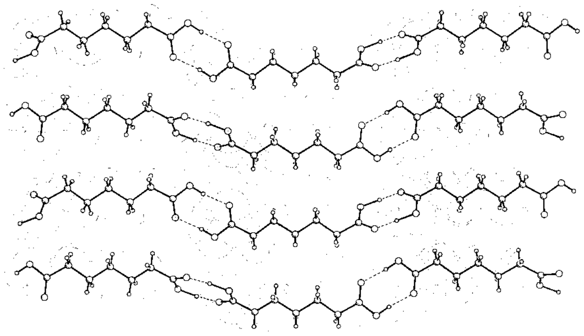

Figure 6. Layer structure in the α-form of C7-diacid. Molecules lie on general positions with a twisted conformation. Lateral molecules are linked through carboxy dimers to form infinite hydrogen bonded chains. Hydrophobic interactions maintain the interchain assembly. Notice the similarity between methylene chain packing with that in Figure 3b and the absence of offset (compare with Figure 5 and contrast with Figure 4). Note that alternating carboxy dimers along the chain and down the column are in inclined planes (contrast with Figure 5).

combination of tilting and offset leads to a different kind of methylene fitting in even diacids from that seen in *n*-alkanes (Figures 3b and 3c).

Odd Members − α- and *β*-Modifications. Odd diacids crystallize in two modifications generally termed α and *β*.[13] From $C_n \geq 5$ the crystal structures of *β*-forms of odd diacids are similar, so are those of α-forms (Tables 2 and 3). The crystal packing details of odd diacids are described using C7-diacid as a representative example. The crystal structures of *β*- and α-modifications of C7-diacid are displayed Figures 5 and 6, respectively. Whereas the molecules are bisected by crystallographic 2-fold axes in the *β*-form, they are located on general positions in the α-form. As in the even members, layer structures are found in both the modifications of odd members wherein (a) the molecules are laterally linked through carboxy dimers to form infinite hydrogen bonded chains and (b) the interchain aggregation is maintained by hydrophobic interactions between methylene groups. There is a difference between the chain aggregation in α- and *β*-forms. While the adjacent hydrogen bonded chains in the *β*-form are translation related, they are inversion related in the α-form.

Some important differences exist between the layer structures of even and odd members (Figures 4, 5, and 6). The molecules in both modifications of the odd members are *not* offset along the chain axis as in the even members. The non-offset situation leads to a hydrophobic fit of methylene groups similar to that seen in *n*-alkanes (Figure 3b). Unlike in the even members, the interchain separations in *β*- (4.7 Å) and α-forms (4.8 Å, data from 298 K) of odd members are comparable to that in *n*-alkanes (4.7 Å). The attention may now be focused on the most important distinction between even and odd structures. The carboxy groups in both modifications of odd diacids turn out-of-plane with respect to the methylene chains (Table 4, Figures 5 and 6). In *β*-form the two carboxy groups twist to an equal and opposite extent with respect to the chain. In α-form, although the two carboxy groups turn in opposite directions, one of the carboxy groups twists to a greater extent than the other. The overall mutual inclination between the two carboxy planes is, however, similar in both modifications (∼60°). This is completely contrary to the situation in the even members where the twist of carboxy groups is negligibly smaller (Table 4). The twisting of carboxy groups in the odd members distorts the molecule as a whole and introduces severe torsions into the carbon chains (Table 5). From the torsion angles recorded in Table 5 it may be noted that the torsions at the end of the chain are greater than those at the center. This clearly indicates that the origin of the torsions lies in the twisting of carboxy groups. What is important in the context of melting point alternation is that high torsions in odd members result in energetically unfavorable molecular conformations.[28]

Table 4. Carboxy Group Inclinations and O−H···O Hydrogen Bond Distances in Diacids with $C_n \geq 5$

C_n[a]	∠COO-chain (deg)[b]	∠COO−COO (deg)[c]	O···O
5 (*β*-form)	32.5	63.0	2.663
6	7.1	0.0	2.656
7 (*β*-form)	31.1	61.9	2.659
7 (α-form)[d]	14.6/48.4[e]	62.7	2.664/2.665[e]
8	3.0	0.0	2.638
9 (*β*-form)	31.0	61.9	2.657
9 (α-form)[d,f]	16.3/49.9[e]	66.2	2.662/2.670[e]
10	1.9	0.0	2.635

[a] Number of C-atoms in the molecule. [b] Angle between a carboxy plane and the mean plane of carbon chain. [c] Angle between the planes of two carboxy groups of the molecule. [d] Data collected at 298 K. [e] Two values correspond to two symmetry independent carboxy groups. [f] Data taken from ref 10k.

The energies of the optimized and observed molecular conformations of even and odd diacids are computed with hybrid-DFT methods (B3LYP/6-31G*, see Experimental Section). The differences in the molecular energies of optimized and observed conformations for C5- to C10-diacids are given in Table 5. It is clear from these values that the odd molecules possess higher energy in the solid state conformation than in an ideal isolated state. This difference in energy is released during the process of melting, sublimation, or dissolution and thereby lowers the melting point, sublimation enthalpy, or heat of solution.[2] Thus, strained torsional conformations are responsible for the lower melting points of odd members despite their higher densities and packing coefficients.[29]

The crucial questions which now remain to be answered are: (a) Why are the carboxy groups twisted only in the odd members

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(28) Twisting of carboxy groups also seem to result in somewhat longer hydrogen bonding separations in the odd members. The O···O distances for even and odd diacids are given in Table 4. It may be noted that the differences are at the second decimal place, and the difference in their contribution to the overall packing energy, although detectable, is very little.

(29) The packing coefficients follow a trend similar to that of densities, that is, they are inversely correlated with the melting points. See Tables 2 and 3 and also Supporting Information for a graphical display.

Table 5. Torsion Angles in Diacids with $C_n \geq 5$

C_n[a]	chain numbering[b]	torsion angles[c]	ΔE (kJ mol^{-1})[d]
5 (β-form)	C1−C2−C3−C2′−C1′	10.2, 10.2	2.665
6	C1−C2−C3−C3′−C2′−C1′	5.5, 0.0, 5.5	0.978
7 (β-form)	C1−C2−C3−C4−C3′−C2′−C1′	10.7, 6.0, 6.0, 10.7	2.418
7 (α-form)	C1−C2−C3−C4−C5−C6−C7	3.1, 11.2, 0.9, 7.3	7.356
8	C1−C2−C3−C4−C4′−C3′−C2′−C1′	5.8, 0.3, 0.0, 0.3, 5.8	0.992
9 (β-form)	C1−C2−C3−C4−C5−C4′−C3′−C2′−C1′	9.7, 4.6, 3.4, 3.4, 4.6, 9.7	2.235
9 (α-form)[e]	C1−C2−C3−C4−C5−C6−C7−C8−C9	4.7, 11.2, 0.2, 5.1, 2.1, 3.9	7.499
10	C1−C2−C3−C4−C5−C5′−C4′−C3′−C2′−C1′	3.4, 3.0, 1.3, 0.0, 1.3, 3.0, 3.4	0.791

[a] Number of C-atoms in the molecule. [b] Symmetry-related atoms are labeled with a prime. [c] The first value corresponds to the atoms C1−C2−C3−C4 and the second to C2−C3−C4−C5 and so on. All of the angles are expressed as absolute values. [d] The difference in energies between observed (see text) and B3LYP/6-31G* optimized molecular structures. The values for even members are given in bold for easy distinction. [e] Data taken from ref 10k.

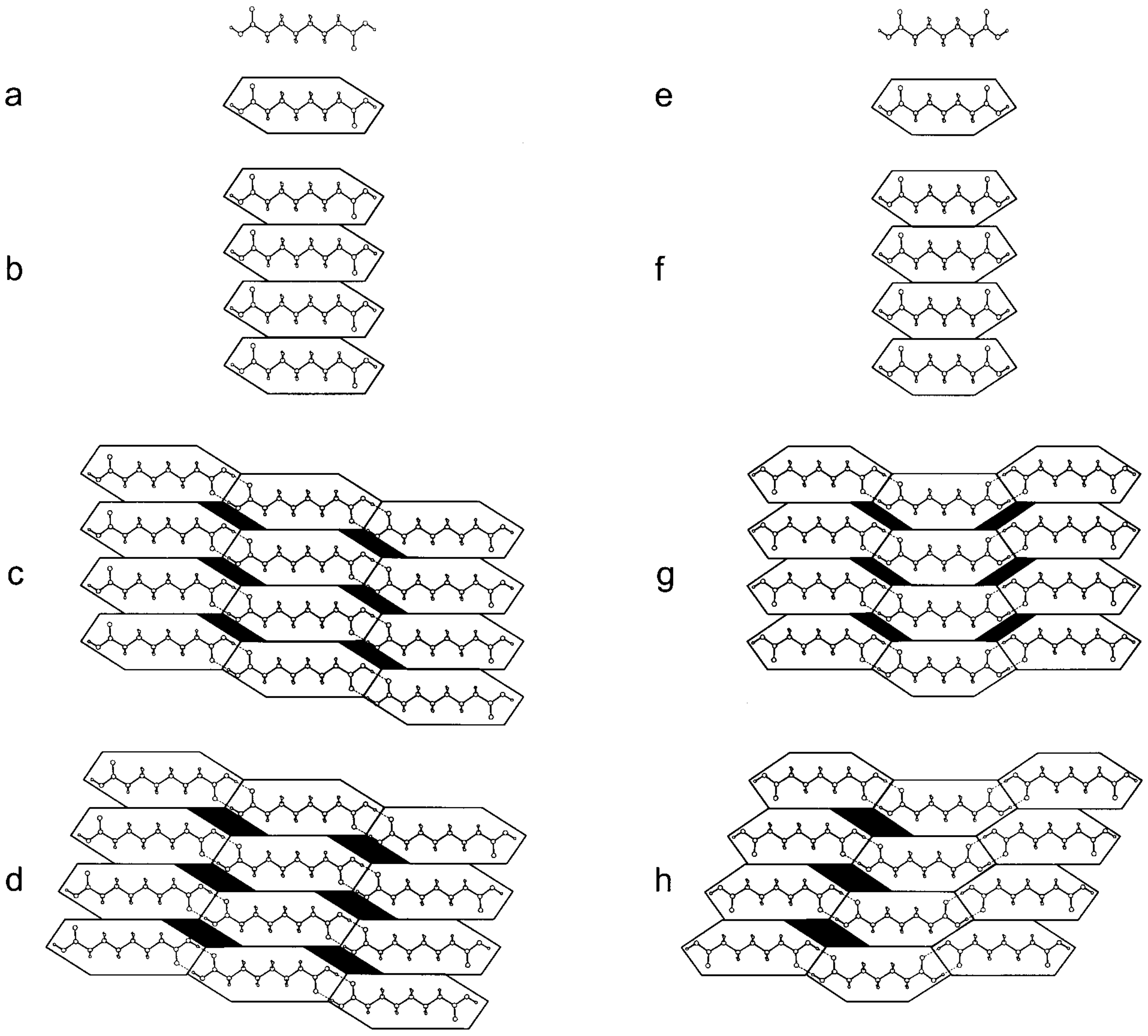

Figure 7. A possible geometrical model for the packing of even (left) and odd (right) diacids in two-dimensions. See text for further details.

(in both modifications)? (b) Why is the offset observed only in the even members? (c) How are "offset−non-twist" and "non-offset−twist" situations related to one another? To answer these questions we adopt the geometrical model described by us previously for *n*-alkanes[14] and dithiols.[16] We mentioned earlier that diacids resemble *n*-alkanes and dithiols in terms of end group connectivity, and in this respect the model described for the latter two series aptly fits to diacid structures.

The Parallelogram−Trapezoid Model. Figure 7 illustrates the model. The even molecules with C_i symmetry and the odd molecules with C_2 symmetry may be depicted as parallelograms and trapezoids, respectively. These geometrical objects are slightly modified (Figure 7a and e), as in the case of dithiols, to accommodate the C−COOH groups and also to reflect the fact that two carboxy groups approach one another in a one-to-one manner. For ease of notation we still call these modified objects parallelograms and trapezoids. If a dense packing of these objects is required in the vertical direction, columnar patterns such as those shown in Figure 7b and f may be obtained. Lateral packing of these columnar patterns may now be considered. Among other possibilities, patterns shown in Figure 7c and g could be obtained in order to account for the observed carboxy dimer synthons. Thus, arrangements shown in Figure 7c and g are driven by two important interactions: hydrophobic packing of methylene chains in the vertical direction and, the hydrogen bonding in carboxy dimers in the horizontal direction. These arrangements, however, force the carboxy dimers of adjacent hydrogen bonded chains into an unfavorable, repulsive proximity. It may be seen from Figure 7c and g that the carboxy dimers cluster around the gaps (shaded in black) at nonbonding distances as short as 1.5 Å. Naturally, the system becomes unstable and tends to advance to a stable situation.

The stability can be achieved by distancing the carboxy dimers from one another. One way of doing this is to slide the objects along the chain axis so that the carboxy dimers are kept away from one another. An offset of parallelograms, as shown in Figure 7d, is possible so that the distance between the carboxy dimers is increased, and thereby the repulsions between them decreased. In principle the parallelograms can be offset until they reach the end of the column. The offset shown in Figure 7d is a situation close to the observed one. At this stage the hydrogen bonded chain as a whole rotates with respect to the meanplane of objects. Such rotation further increases the distance between carboxy dimers and leads to the realistic situation is shown in Figure 4, without any torsional impositions on the molecule.

Consider the offset for trapezoids. As shown in Figure 7h, the offset leads to a situation where the carboxy dimers are separated at one end of the column whereas at the other end the carboxy dimers move much too close to one another. This increases the repulsions to an even greater extent. Offset in both directions of the trapezoid pattern leads to the same result. Offset is therefore not a realistic possibility for the trapezoid pattern, and the molecules are forced to be in a repulsive environment. The odd diacids therefore stick to the pattern shown in Figure 7g, but the carboxy dimers twist away from the planarity to reduce the mutual repulsions from the related dimers of adjacent chains. Twisting of carboxy groups is therefore inevitable in odd diacids (to reduce the repulsions), but it introduces severe torsions into the molecules, thereby incorporates high energy into them and consequently culminates in the lowering of their melting points.

There is another significant effect of carboxy group twisting which is now considered. Twisting in odd diacids causes the two carboxy groups at both ends of a molecule to turn in opposite directions. Two possibilities exist for the interchain arrangement when such a twisting takes place: (a) the dimers at one end of the column are in parallel planes, and (b) the dimers at one end of the column are at inclined orientations. This explains why dimorphism is so prevalent in odd diacids. The possibilities (a) and (b) are realized in the *β*- and α-modifications of odd diacids (Figures 5 and 6) where the corresponding angles of inclinations are 0.0 and 57.0°.[30]

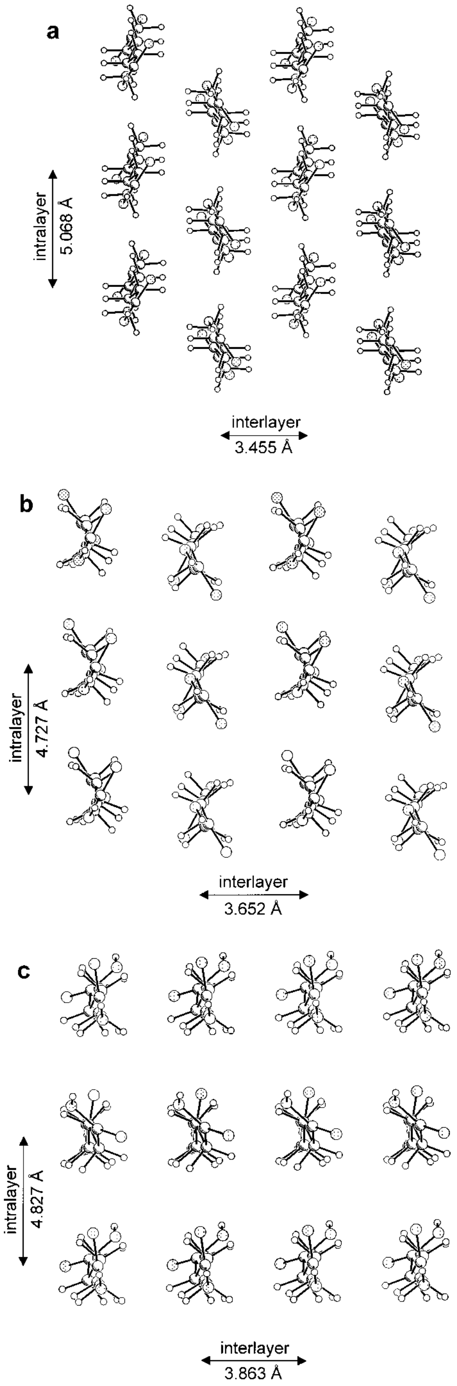

Figure 8. View down the chain axis illustrating the interlayer packing in (a) C8-diacid, (b) *β*-C7-diacid, and (c) α-C7-diacid. Compare these with Figure 3d. Note the torsional conformation in (b) and (c). The distances given for α-C7-diacid correspond to the data at 298 K. Corresponding intra- and interlayer distances respectively for C8- and *β*-C7-diacids at 298 K are 5.063, 4.789, and 3.585, 3.747 Å.

The present model is effective when (a) the molecules stack into columns and (b) when the mutual recognition of end groups takes place in a one-to-one manner. The first factor requires that the alkyl chain length is sufficiently long so that it can provide enough hydrophobic strength to steer the intergrooving pattern. In the present case the model is valid from C5-diacid to the higher members. In the case of *n*-alkanes and dithiols the model is valid from *n*-hexane and 1,4-butanedithiol, respectively. It appears that a minimum of three to four methylene groups is required to steer the molecules into columns. If the chain is shorter, the hydrophobic strength is not enough to form columns, and therefore the model does not suit lower members. The second factor requires that each end group is connected to only one other end group. In the present case the carboxy groups form dimers, that is, each group is linked to one other group only, and therefore the model is applicable. If the carboxy groups were to form catemers, in which case each group is linked to two others, the model requires to be modified to take into account the second connectivity. Another important requirement is that geometrical interference between the interaction patterns of chain and the end groups should be a minimum or they should

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[30] Many other possibilities could be imagined with various degrees of inclination of adjacent dimers, but only those possibilities are realized which confer stability to the overall packing. Further polymorphs suggested in a recent study (ref 12m) could well belong to one of these possibilities.

be insulated from one another. In the present case the carboxy dimers and hydrophobic packing occur in distinct domains which allows for the adaptability of the model.

The parallelogram−trapezoid model is widely applicable, and its generality can be appreciated for the following reasons: (a) In *n*-alkanes it explains why the end (CH_3) groups in the odd members approach to non-equal distances as opposed to the equally spaced end groups in the even members.[14] (b) In dithiols it demonstrates why an offset toward higher density is allowed in even members and forbidden in odd members.[16] In these two cases the higher packing density confers greater melting enthalpy, and therefore the melting points of even members are higher than those of odd members. (c) In the present series it illustrates why "offset−non-twist" and "non-offset−twist" situations are seen in even and odd members, respectively, and uncovers the reasons for the molecular strain in the odd members which lowers their melting points. The model is fairly robust, and it logically explains the reasons for the differences between the structures of even and odd members on the basis of their geometry. We note that our model is not intended to predict, define, or even rationalize melting point of an individual compound.

Interlayer Packing. The parallelogram−trapezoid model described above is two-dimensional, and consideration of interlayer association (Figure 8) reveals the packing in third dimension. Adjacent layers are glide related in the even members (Figure 8a), whereas they are inversion related in β- (Figure 8b) and translation related in α-forms (Figure 8c) of odd diacids. Intralayer separations in the even members are longer than those present in both modifications of the odd members. An exactly opposite situation prevails for the interlayer separations. Even members adopt long intralayer separations to reduce the repulsions between carboxy dimers of adjacent chains. This is compensated by compact interlayer packing. The interlayer packing is somewhat looser in the odd members which alleviates the repulsions between carboxy dimers in the interlayer region. Within odd members, the packing of β-forms is denser than that of α-forms.

Conclusions

Crystal structural analyses of C2- to C10-diacids have been carried out at 130 and 298 K which resolved previous misconceptions relating their structures and melting points. Solid-state densities and melting points of diacids exhibit alternating trends, but they are inversely correlated with one another. Closest packing is therefore not the reason for a higher melting point as in the previously described cases of *n*-alkanes, dithiols, diols, and diamines where the alternating trends of densities and melting points are in line. In this context diacids represent an entirely different scenario. Even diacids and dimorphic odd diacids display gross structural similarities with carboxy groups forming hydrogen bonded dimers and methylene chains aggregating into hydrophobic columnar patterns. Whereas the carboxy groups turn out of the molecular plane in both modifications of odd diacids leading to energetically unfavorable twisted molecular conformations, they remain in the molecular plane in even members. It is shown, with the help of a simple, geometry-based parallelogram−trapezoid model, that crystal packing requirements of odd diacids impose restrictions on molecular conformations which inevitably lower the melting points of odd members, leading to the observed melting point alternation. In other words, the necessities of supramolecular aggregation lead to molecular deformations in odd diacids.

Although melting is a poorly understood phenomenon,[31] it is generally considered to arise from the disassociation of solid-state molecular assembly. That is, melting is related to intermolecular association. It is shown here that the structure of individual molecules also plays a very important role in melting. It may be said that those solid-state structures in which molecules are associated with energetically unfavorable geometries would have lower melting points than related structures with ideal molecular geometries. The present work establishes reliable connections between structures of diacids and their melting points and has important implications in the structure−property relationships in the homologous series of *n*-alkanes and derivatives in particular, and structural chemistry in general.[32] Further studies are in progress to unfold the reasons for alternating physical properties in many other *n*-alkane derivatives.

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Supporting Information Available: Figures of density and packing coefficient trends and tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for all the diacids at 130 and 298 K (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[31] Cotterill, R. M. J. (*J. Cryst. Growth* **1980**, *48*, 582) eloquently expresses the following in his article entitled "The Physics of Melting": "It is interesting to note that of all the physical phenomena known to man, some of the most common have proved to be the most difficult to understand. Melting is a case in point. The ultimate transition from the crystalline state to the liquid state, at a sufficiently high temperature, remains a mystery."

[32] Our work is largely confined to providing an answer to the alternating melting point riddle well-known in *n*-alkanes and their derivatives. However, the even−odd carbon atom disparity is much more general (see: Sarma, J. A. R. P.; Nangia, A.; Desiraju, G. R.; Zass, E.; Dunitz, J. D. *Nature* **1996**, *384*, 320).