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

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Abstract: α,ω-Alkanedithiols show an alternation in their melting points with even members exhibiting systematically higher melting points than odd members. In this study, single crystals of the first nine members of α,ω-alkanedithiols ($HS-(CH_2)_n-SH$, $n = 2-10$) have been grown in situ using a miniature zone melting procedure, and their X-ray analyses have been performed. The structural similarities and differences between even and odd members have been analyzed based on the packing arrangements of hydrocarbon chains and SH functionalities. Whereas the hydrocarbon chains maintain an intergrooving pattern, the SH groups associate in an antiparallel fashion in both the members. The SH groups do not form hydrogen bonds. In the even members the molecules are offset along their length, whereas such an offset is not observed in the odd members. The densities of even members are systematically higher than those of odd members and show an alternating trend. Using a simple geometrical model, describing even and odd members as modified parallelograms and trapezoids, respectively, the density features of the packing patterns in both the members are illustrated. The melting point alternation in dithiols is attributed to the geometry allowed or forbidden molecular offset toward a higher packing density.

Introduction

n-Alkanes and most of the end-substituted *n*-alkanes show a remarkable alternation in their melting points.[1,2] The even members exhibit systematically higher melting points than the odd members. Although physical properties such as solubilities and sublimation enthalpies that are related to the solid state also exhibit an alternating pattern, those related to the liquid state show a monotonic behavior.[1] This fact is so well-known that it appears in almost all standard chemistry text books, *but* it has received no plausible explanation thus far. Because the alternation is a phenomenon pertaining to the solid state, any such explanation requires precise crystal structural data. The difficulties in growing single crystals of most of these compounds have precluded the efforts in this direction.

Recently, we showed that the melting point alternation in *n*-alkanes can be explained based on a geometrical model.[3] The structures of *n*-alkanes are held together solely by hydrophobic interactions. The two structure types observed for even and odd members of triclinic *n*-alkanes can be distinguished on the basis of unlike intermolecular interactions around the end groups, the methyl groups. In our quest to understand the effects of various functional groups on the structural attributes of *n*-alkanes, we have determined the crystal structures of α,ω-alkanedithiols (dithiols hereafter) $HS-(CH_2)_n-SH$, $n = 2-10$. The structural chemistry of thiols has not been exploited, and we present here our results based on the structural analysis of nine dithiols. In a general sense, understanding the crystal-packing behavior of alkyl chains and SH groups has important implications in material[4] (monolayer self-assembly, soft-lithography, molecular recognition at interfaces, crystal growth, liquid crystals, conduction) and biological[5] (protein folding, drug-receptor recognition, membrane transport) phenomena.

Experimental Section

1,7-Heptane- and 1,9-nonanedithiols were synthesized according to reported procedures and were purified by distillation.[6] The other dithiols reported here were commercially available and were used for crystal growth as received. Because all these compounds are liquids at room temperature, single crystals were grown in situ using a miniature zone melting procedure.[7] In a typical experiment, the liquid sample was taken in a sealed quartz capillary and cooled below its melting temperature very slowly on the diffractometer so that it became polycrystalline. A tunable fine-focused IR laser was applied at appropriate intensity to melt the sample and then scanned along the length of the capillary. Several cycles of scanning results in a single crystal suitable for X-ray diffraction.[8]

The X-ray data were collected at 130 K on a Nicolet R3 diffractometer using Mo−Kα radiation and were corrected for the cylindrical shape of the crystal. The structure solutions and refinements were performed using SHELX programs built in with the SHELXTL-5.03 suite.[9] All the H-atoms were located from the difference Fourier maps and

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[†] The Melting Point Alternation in *n*-Alkanes and Derivatives, Part 3. For parts 1 and 2 see refs 3 and 19, respectively.

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(6) Hall, W. P.; Reid, E. E. *J. Am. Chem. Soc.* **1943**, *65*, 1466.

(7) Boese, R.; Nussbaumer, M. In *Correlations, Transformations, and Interactions in Organic Crystal Chemistry, IUCr Crystallographic Symposia*; Jones, D. W., Katrusiak, A., Eds.; Oxford University Press: Oxford, 1994; Vol. 7; pp 20−37.

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10.1021/ja993422l CCC: $19.00

Table 1. Crystallographic Data for Dithiols

C*n*[a]	2	3	4	5	6	7	8	9	10[b]
emp. form.	$C_2H_6S_2$	$C_3H_8S_2$	$C_4H_{10}S_2$	$C_5H_{12}S_2$	$C_6H_{14}S_2$	$C_7H_{16}S_2$	$C_8H_{18}S_2$	$C_9H_{20}S_2$	$C_{10}H_{22}S_2$
form. wt.	94.19	108.21	122.24	136.27	150.29	166.33	178.34	192.37	206.40
mp (°C)	−41.2	−79	−53.9	−72.5	−21	−38.1	0.9	−17.5	20
T (K)[c]	130	130	130	130	130	130	130	130	130
cryst. syst.	orthorhombic	orthorhombic	triclinic	monoclinic	triclinic	monoclinic	triclinic	monoclinic	triclinic
space group	Pbca	$P2_12_12_1$	$P\bar{1}$	$P2/c$	$P\bar{1}$	$P2/c$	$P\bar{1}$	$P2/c$	$P\bar{1}$
a (Å)	7.283(2)	5.9932(2)	4.037(1)	8.085(2)	4.053(3)	10.447(2)	4.0784(12)	12.191(5)	4.2100(8)
b (Å)	5.9330(12)	9.434(2)	5.3407(12)	4.5487(10)	5.364(4)	4.5641(11)	5.3612(14)	4.579(2)	5.4200(11)
c (Å)	10.537(2)	9.733(2)	7.452(2)	10.636(2)	9.713(9)	10.708(2)	11.623(3)	10.709(3)	13.610(3)
α (°)	90	90	80.44(2)	90	105.06(6)	90	81.12(2)	90	90.14(3)
β (°)	90	90	87.92(2)	109.09(2)	93.36(6)	115.151(14)	81.67(2)	111.69(3)	96.85(3)
γ (°)	90	90	86.97(2)	90	93.41(5)	90	86.27(2)	90	96.04(3)
Z	4	4	1	2	1	2	1	2	1
V (Å^3)	455.3(2)	550.3(2)	158.15(7)	369.7(2)	202.9(3)	462.2(2)	248.20(12)	555.4(4)	306.59(1)
D_{calc} (Mg/m^3)	1.374	1.306	1.283	1.224	1.230	1.195	1.193	1.150	1.118
F (000)	200	232	66	148	82	184	98	212	114
2*θ* range	7.74−90.18	6.02−59.98	5.54−59.98	5.34−60.04	4.36−60.34	3.30−60.02	3.58−60.58	3.60−60.00	
index ranges	$-10 \le h \le 14$ $-8 \le k \le 11$ $-8 \le l \le 20$	$-8 \le h \le 6$ $-13 \le k \le 13$ $-10 \le l \le 13$	$-5 \le h \le 5$ $-7 \le k \le 7$ $-10 \le l \le 10$	$-11 \le h \le 2$ $-6 \le k \le 3$ $-14 \le l \le 14$	$-5 \le h \le 5$ $-7 \le k \le 7$ $-13 \le l \le 2$	$-13 \le h \le 9$ $-6 \le k \le 1$ $-15 \le l \le 1$	$-5 \le h \le 5$ $-7 \le k \le 7$ $-16 \le l \le 0$	$-17 \le h \le 17$ $-5 \le k \le 4$ $-15 \le l \le 15$	
R_1	0.044	0.033	0.028	0.026	0.025	0.041	0.029	0.061	
wR_2	0.115	0.090	0.051	0.071	0.070	0.113	0.081	0.170	
GOF	1.051	1.087	1.087	1.145	1.124	1.108	1.075	1.120	
N-total[d]	3025	2915	1864	2155	1521	1561	1524	2605	
N-indep.[e]	1875	1601	932	1086	1199	1146	1458	1466	
N-obsd.[f]	1441	1540	903	1026	1167	1144	1383	1155	
variables	31	78	48	57	65	74	74	91	
C_k*[g]	0.691	0.681	0.697	0.672	0.698	0.675	0.695	0.669	

[a] Number of C-atoms in the molecule. [b] The quality of the data obtained is not good enough to present refinement details. [c] Temperature of the data collection. [d,e] Number of collected and independent reflections. [f] Number of observed reflections based on the criteria $I > 2\sigma_I$. [g] Packing coefficient.

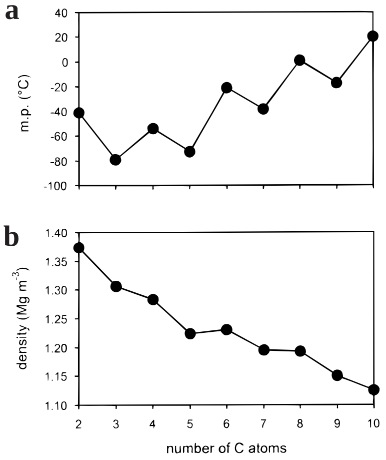

Figure 1. The melting point (a) and the density (b) alternation in dithiols.

were refined isotropically. Table 1 gives salient crystallographic details, and further information is provided in the Supporting Information.

Results and Discussion

The melting point alternation of dithiols is shown in Figure 1a. All the melting points were recorded using differential scanning calorimetry, and no indication of phase transitions was observed. The X-ray data (Table 1) for all the compounds were collected at the same temperature to allow for the comparison of calculated densities. Density gives a measure of compactness, and in a homologous series it may be correlated with melting point.[3] It is evident from the density alternation (Figure 1b) that the odd dithiols are poorly packed. The densities decrease with increasing chain length because of the increased hydrophobic content.

The reasons for the alternating trend of solid state physical properties of even and odd dithiols are expected to be embodied in the crystal-packing arrangements. Accordingly, we are required to understand the structural characteristics of these compounds. A worthwhile strategy in the rationalization of crystal structures is to glean the possible interaction patterns of different functional groups from the existing data and then to understand the mutual effects of these patterns when they are used in a given system.[10] Geometrical and chemical factors come into play, and from the crystal structures of a series of similar compounds it is possible to trace recurring robust interaction patterns, the supramolecular synthons.[11] Dithiols are made of hydrocarbon chains and SH groups, and our analysis takes the form of finding packing patterns that are likely for these two sets of functionalities and their mutual interplay.

A knowledge of the hydrophobic packing in *n*-alkanes is helpful. Molecular packing along their lengths is similar in even and odd members of *n*-alkanes and is illustrated in Figure 2 with the structure of *n*-hexane.[3] An orthogonal notation (Figure 2a) 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 the *xy*-plane. Methylene groups of successive molecules intergroove along *y* at a distance of 4.7 Å and produce a columnar structure (Figure 2b). These columns stack over one another perpendicular to the molecular plane (Figure 2c). The molecules slide along the chain axis (*x*) such that the projections fit into hollows. Two kinds of patterns typically are observed (Figures 2b and 2c). The significance of these patterns will become apparent in understanding the packing of hydrocarbon chains in dithiols.

The crystal-packing behavior of SH groups has not been explored.[12] The total number of crystal structures of organic compounds with SH groups deposited in the Cambridge Structural Database (April 1999 release, 197481 crystal structures)[13]

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(9) Sheldrick, G. M. *SHELXTL Version 5.03. An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data*; Bruker AXS: Madison, Wisconsin, USA, 1997.

(10) Desiraju, G. R. *Crystal Engineering: The Design of Organic Solids*; Elsevier: Amsterdam, 1989.

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

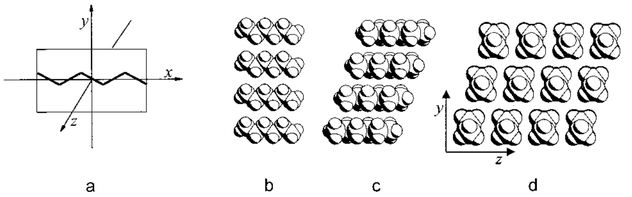


Figure 2. Main chain packing in *n*-hexane. (a) A schematic representation for the packing in three dimensions. Note that *x, y,* and *z* are not crystallographic axes. The chain axis, *x*, passes through midpoints of all the C−C bonds. (b) Intergrooving pattern of methylene groups along *y*. Successive 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 the molecules are projected on the plane of the paper in this and all other figures.

is only 115. Many of these structures consist of other functional groups capable of forming strong hydrogen bonds such as O−H···O, N−H···O, and O−H···N. Because the crystal packing is dominated by strong hydrogen bonds in general, it is difficult to decipher the packing features of the SH groups from these structures. There have been some reports related to hydrogen bonding by SH as a donor, and also S (in the form of thiol, thioether, or thione) as an acceptor.[14] In the present structures the possible hydrogen bonds are of the S−H···S and C−H···S type. In his seminal book on crystal engineering Desiraju noted the ambivalent nature of sulfur in its involvement in isotropic and directional interactions.[10] Clearly, the existing data are insufficient to predict the supramolecular behavior of SH groups.[15] The present study deals with crystal structures of nine dithiols that contain C, H, and S as the constituent elements and provides a greater scope for the understanding of the packing characteristics of SH groups in a relatively noncompetitive environment.

Dithiols with $C_n \geq 4$ crystallize in the space groups $P\bar{1}$ for even members and $P2/c$ for odd members with systematic gradations in their unit cell parameters. Molecular symmetry is extended to the crystal symmetry in both cases. Molecules are located on inversion centers in the even members and they are bisected by 2-fold axes in the odd members. The similarity in the space groups within even or odd members immediately suggests the similarity in their packing patterns. Dithiols with $C_n = 2$ and 3 do not follow this trend and crystallize in the space groups *Pbca* and $P2_12_12_1$, respectively. The following discussion is applicable for dithiols with $C_n \geq 4$.

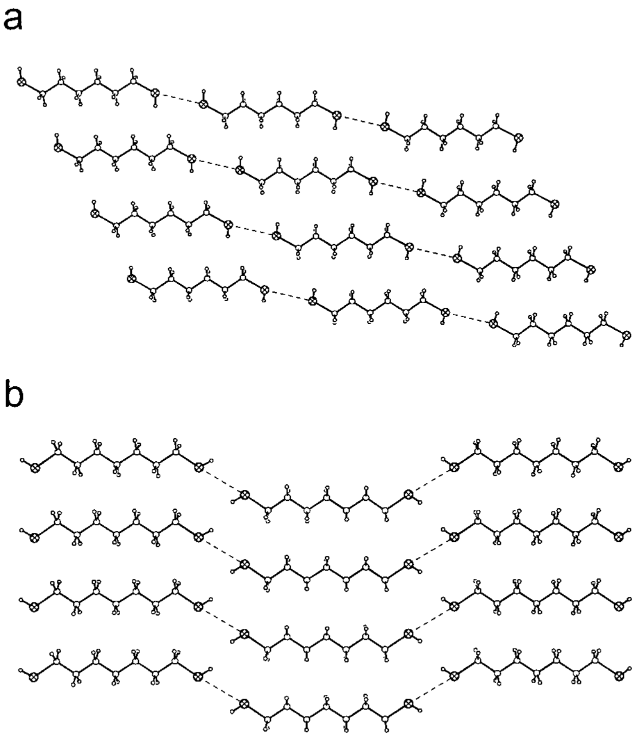
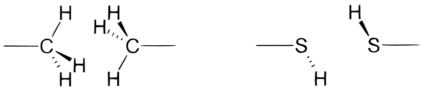


Figure 3. Layer structures in 1,6-hexanedithiol (a) and 1,7-heptanedithiol (b). Notice the intergrooving pattern and the close approaches of SH groups in an antiparallel fashion as shown in Scheme 1. Notice that the even dithiol molecules within a column are offset along the chain axis (toward right in the figure). The offset (2.8 Å) is driven by the fit of both the SH groups into the hydrophobic grooves of methylene groups. Notice the absence of offset in odd dithiols.

Figure 3 displays the layer structures in even and odd dithiols. In both cases columnar patterns sustained by the intergrooving of methylene groups are observed. The SH groups associate across the inversion centers in both cases. The S···S distances are similar in both cases and range from 3.48 to 3.51 Å (slightly shorter than the van der Waals separation, 3.6 Å).[16] However, the C−S···S angles are more linear in odd members (∼173°) than the even ones (∼162°).[17] The mutual recognition of SH groups in dithiols is similar to that of CH_3 groups in *n*-alkanes, and the recognition takes place in a specific manner leading to an antiparallel association of SH groups (Scheme 1). Such specificity toward antiparallel arrangement endows directionality to the C−S···S−C geometries.[18]

Scheme 1. Self-recognition Supramolecular Synthons of CH_3 and SH Groups. Notice that Each Group Associates with Only One Other Group



Some noticeable differences exist between the layer structures of even and odd dithiols. In the even members the adjacent molecules in a column are offset along the chain axis (Figure 3a). The offset is driven by the fit of SH groups into the grooves formed by methylene groups, at both ends of the molecule. If the offset were to take place in the opposite direction (toward left instead of right as observed in Figure 3a), the SH groups

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(12) For early accounts of the structural chemistry and the hydrogen bonding by thiol group, see (a) Paul, I. C. In *The Chemistry of the Thiol Group*, Part 1; Patai, S., Ed.; John Wiley: London, 1974; pp 111−149. (b) Crampton, M. R. In *The Chemistry of the Thiol Group*, Part 1; Patai, S., Ed.; John Wiley: London, 1974; pp 379−415.

(13) Allen, F. H.; Davies, J. E.; Galloy, J. J.; Johnson, O.; Kennard, O.; Macrae, C. F.; Mitchell, E. M.; Mitchell, G. F.; Smith, J. M.; Watson, D. G. *J. Chem. Inf. Comput. Sci.* **1991**, *31*, 187.

(14) (a) Mallinson, P. R.; MacNicol, D. D.; McCormack, K. L.; Yufit, D. S.; Gall, J. H.; Henderson, R. K. *Acta Crystallogr.* **1997**, *C53*, 90. (b) Pedireddi, V. R.; Chatterjee, S.; Ranganathan, A.; Rao, C. N. R. *J. Am. Chem. Soc.* **1997**, *119*, 10867. (c) Narayanan, S. J.; Sridevi, B.; Chandrashekar, T. K.; Vij, A.; Roy, R. *Angew Chem., Int. Ed. Engl.* **1998**, *37*, 3394. (d) Rozenberg, M. S.; Nishio, T.; Steiner, T. *New J. Chem.* **1999**, *23*, 585. (e) Desiraju, G. R.; Steiner, T. *The Weak Hydrogen Bond in Structural Chemistry and Biology*; Oxford University Press: Oxford, 1999; pp 253−266.

(15) The directional preferences of intermolecular interactions of divalent sulfur (excluding thiols) with various other electrophilic or nucleophilic species have been studied. See (a) Rosenfield, R. E.; Parthasarathy, R.; Dunitz, J. D. *J. Am. Chem. Soc.* **1977**, *99*, 4860. (b) Row: T. N. G.; Parthasarathy, R. *J. Am. Chem. Soc.* **1981**, *103*, 477.

(16) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(17) The values given are averaged over the structures reported for even ($C_n = 4$, 6, and 8) or odd ($C_n = 5$, 7, and 9) dithiols.

(18) Note that we are dealing with S···S interactions between SH groups, whereas S···S interactions reported in the literature dealt either with thioether or thione functionalities. (See refs 10 and 15b; also (a) Munakata, M.; Wu, L. P.; Kuroda-Sowa, T. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 1727. (b) Nyburg, S. C.; Faerman, C. H. *Acta Crystallogr.* **1985**, *B41*, 274.)

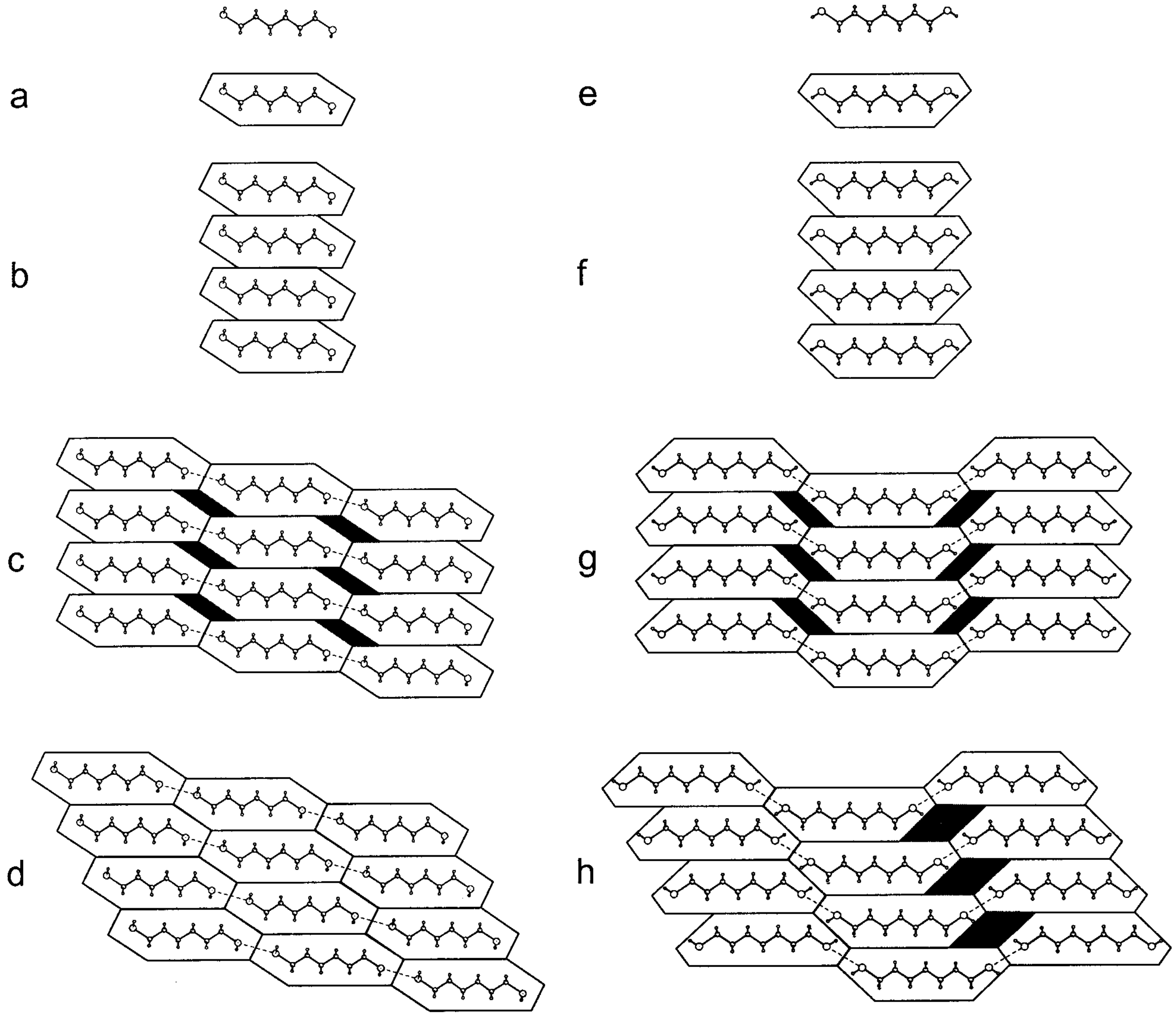

Figure 4. A possible geometrical model for the packing of even (left) and odd (right) dithiols in two dimensions. In reality, the even members adopt the dense packing pattern (d), whereas the odd members restrict to the pattern (g). See text for further details.

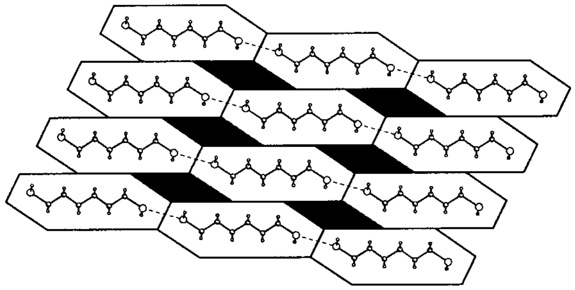

Figure 5. Hypothetical reversed offset in even dithiols. Note the gaps in the intercolumnar region. Compare this with Figures 4c and 4d.

would then stick out of the column, allowing them to form other intermolecular interactions[19] (see below, Figure 5). Accordingly, the direction of the offset is also important. No offset is observed in the odd members (Figure 3b). Thus, we are left with the questions: Why is the molecular offset observed only in the even members? How does it influence the density and the packing efficiency?

To explain this we adopt the planar geometrical model we described for *n*-alkanes but with some further refinements (Figure 4). The even members with C_i symmetry and the odd members with C_2 symmetry may be depicted as parallelograms and trapezoids, respectively.[3] These geometrical objects are slightly modified as shown in Figures 4a and 4e to reflect the fact that a C−S bond is longer than a C−C bond and that two SH groups approach one another in a specific way. 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 Figures 4b and 4f may be obtained. At the molecular level, this is governed by the methylene intergrooving. Lateral packing of these columnar patterns may now be considered. Among other possibilities, patterns shown in Figures 4c and 4g could be obtained to account for the observed recognition of SH groups. Because the increase in molecular length is monotonic in a homologous series (1.27 Å per methylene group), the increase in molecular volume (in the two-dimensional case here, the increase in the area of the objects) would also be monotonic,

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(19) Such a reversed offset is observed in the even members of α,*ω*-alkanediols and α,*ω*-alkanediamines wherein the end groups control the structure through O−H···O and N−H···N hydrogen bonds, respectively. (Thalladi, V. R.; Boese, R.; Weiss, H. C. *Angew. Chem., Int. Ed. Engl.*, in press). The fact that dithiols do not follow the packing patterns similar to those of α,*ω*-alkanediols and α,*ω*-alkanediamines indicates the reluctance of SH groups to participate in S−H···S hydrogen bonding. However, the SH groups in dithiols also form S−H···S contacts, but these are long (H···S, 2.94−3.19, S···S, 3.91−4.08 Å; and S−H···S, 135−154°) and are probably insignificant.

and patterns similar to those shown in Figures 4c and 4g (with similar void space in even and odd ones) would lead to a monotonic trend in the density, but this is not the case.

The gaps in the pattern shown (in black) in Figure 4c are periodic. Obviously, a pattern with no gaps would be denser. This can be achieved by sliding the objects horizontally. As shown in Figure 4d the offset of the objects eliminates the gaps in the pattern of parallelograms and therefore culminates in maximum density for even members. Now consider the offset of trapezoids. It creates a new pattern of trapezoids with new gaps (Figure 4h) and the overall void space is equal to that present in the pattern without the offset (Figure 4g). The gaps in the trapezoid pattern are inevitable, and in reality the odd members adopt the packing depicted in Figure 4g. Thus the odd members are less densely packed than their even analogues, have less packing efficiency,[20] and consequently have lower melting points. Implicit here is the assumption that the melting point is controlled by melting enthalpy and that the density correlates with enthalpy in this homologous series. The melting point alternation of dithiols can thus be explained on the basis of geometry-allow or -forbid molecular offset toward a higher packing density.

Earlier we referred to the direction of the offset in even members. Consider Figures 4c (no offset, hypothetical), 4d (observed offset), and Figure 5 (reversed offset, hypothetical). An offset in the direction opposite (Figure 5) to the observed one would lead to large empty gaps in the intercolumnar region into which SH groups are exposed. Such a loose packing is not favored for obvious reasons. In the odd members the offset in both the directions would lead to the same packing, and the offset in one direction is displayed in Figure 4h.

The present model is two-dimensional and consideration of interlayer association (Figure 6) reveals the packing in the third dimension. In the even members, the layers are translated (Figure 6a), and the model can be extended directly to the third dimension. In the odd members, adjacent layers are inverted and displaced (Figure 6b) to fill the gaps partially in the third dimension. Because the SH groups are slightly larger than the methylene groups and because they are intergrooved into adjacent molecules, intermolecular separation within the columns in the even members is slightly longer (~4.73 Å) than that in the odd members (~4.57 Å).[17] Such slight widening is compensated by compact interlayer packing and by molecular tilt in the even members.

The model described above hinges on two important factors: (1) intergrooving hydrophobic packing can occur only along the length of the molecules and is preferred to other possible nonintergrooving patterns, (2) 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 that it can provide enough hydrophobic strength to steer the intergrooving pattern. In the present case, the model is valid from 1,4-butanedithiol to the higher members. The second factor requires that the end groups are involved in self-recognition and that each end group is supramolecularly linked to only one other end group (Scheme 1). Further modifications of the model will be required when an end group is linked to two or more end groups in the intermolecular region. Efforts in this direction are expected to unravel common packing models based on the supramolecular connectivity of a given end group. Another important factor that is to be considered is the interference between the interaction patterns formed by the chain and the end groups. In the present case, the two patterns are insulated from one another. Indeed, it is this insulation that allows for the development of the described model.

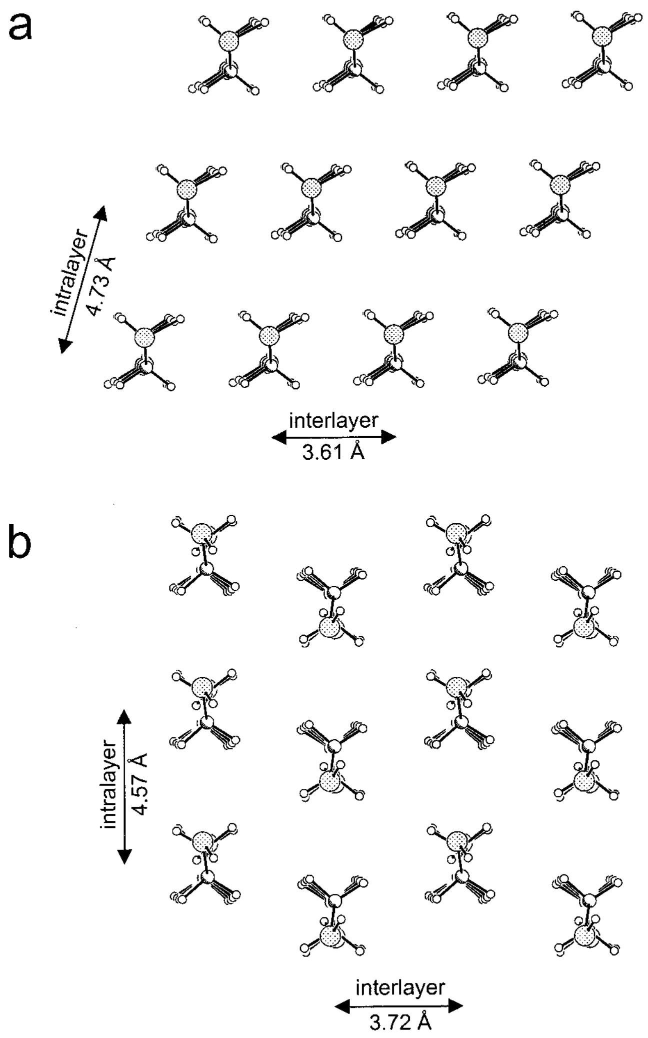

Figure 6. View down the chain axis illustrating the interlayer packing in 1,6-hexanedithiol (a) and 1,7-heptanedithiol (b). Compare these with Figure 2d.

We conclude that (a) in hydrophobic systems such as those described here the SH groups prefer to self-associate in an antiparallel manner rather than forming S−H···S hydrogen bonds, (b) the intergrooving pattern of methylene groups is a dominant packing for hydrocarbon chains, (c) a simple parallelogram−trapezoid model based on the molecular geometry and on the self-recognition of the end groups explains the density features of the packing patterns of α,ω-disubstituted *n*-alkanes, (d) the even members of dithiols have higher melting points than the odd members because their molecular geometry enables an offset toward higher packing density.

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Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for all the dithiols reported (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[20] The calculated packing coefficients (C_k*, Table 1) also show an alternating trend similar to that of densities and melting points.