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# The Crystal Structures of 6-N-Heptylmercaptopurine at 123 K and 6-N-Hexylaminopurine at 295 K

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6-N-Heptylmercaptopurine, $C_{12}H_{18}N_4S$, (I), is monoclinic, $P2_1/c$, $Z = 4$, with cell dimensions at 123 K [295 K] of $a = 15.527(7)$ [15.219(7)], $b = 7.140(3)$ [7.275(3)], $c = 11.979(6)$ [12.414(7)] Å, $\beta = 101.21(4)$ [100.15(4)]°.

6-N-Hexylaminopurine, $C_{11}H_{17}N_5$, (II), is triclinic, $P\bar{1}$, $Z = 2$, with cell dimensions $a = 5.210(10)$, $b = 8.466(13)$, $c = 13.932(10)$ Å, $\alpha = 97.03(16)$, $\beta = 92.03(7)$, $\gamma = 104.43(17)$°.

In the crystal structure of I the molecular packing is head-to-head bilayer with double stacks of purine moieties and interdigitating alkyl chains. This structure is isostructural with the long-chain alkyl pyranosides. In II, the hydrogen-bonded purine residues are packed in imbricated layer structure with antiparallel twisted alkyl chains which are not intercalated. Only structure II shows evidence of thermotropic crystal-to-crystal phase transitions in both heating and cooling cycles; neither crystal forms a liquid crystal phase and both melt directly to an isotropic liquid.

## INTRODUCTION

The long-chain alkyl purines and pyrimidines are amphiphilic molecules analogous to the long-chain pyranosides.[1] They might therefore be expected to have similar physical properties, in particular functioning as cell membrane detergents and forming lyotropic and thermotropic liquid crystals.

The two compounds studied in this work, 6-N-heptylmercaptopurine, I, and 6-N-hexylaminopurine, II, exhibits no liquid crystal phases. As shown by the DSC thermograms (Figure 1), compound II, m.p. 178.3°C, shows phase transitions at 141.7° on the heating cycle and 114.2°C on the cooling cycle. Compound I, m.p. 109.3°C,

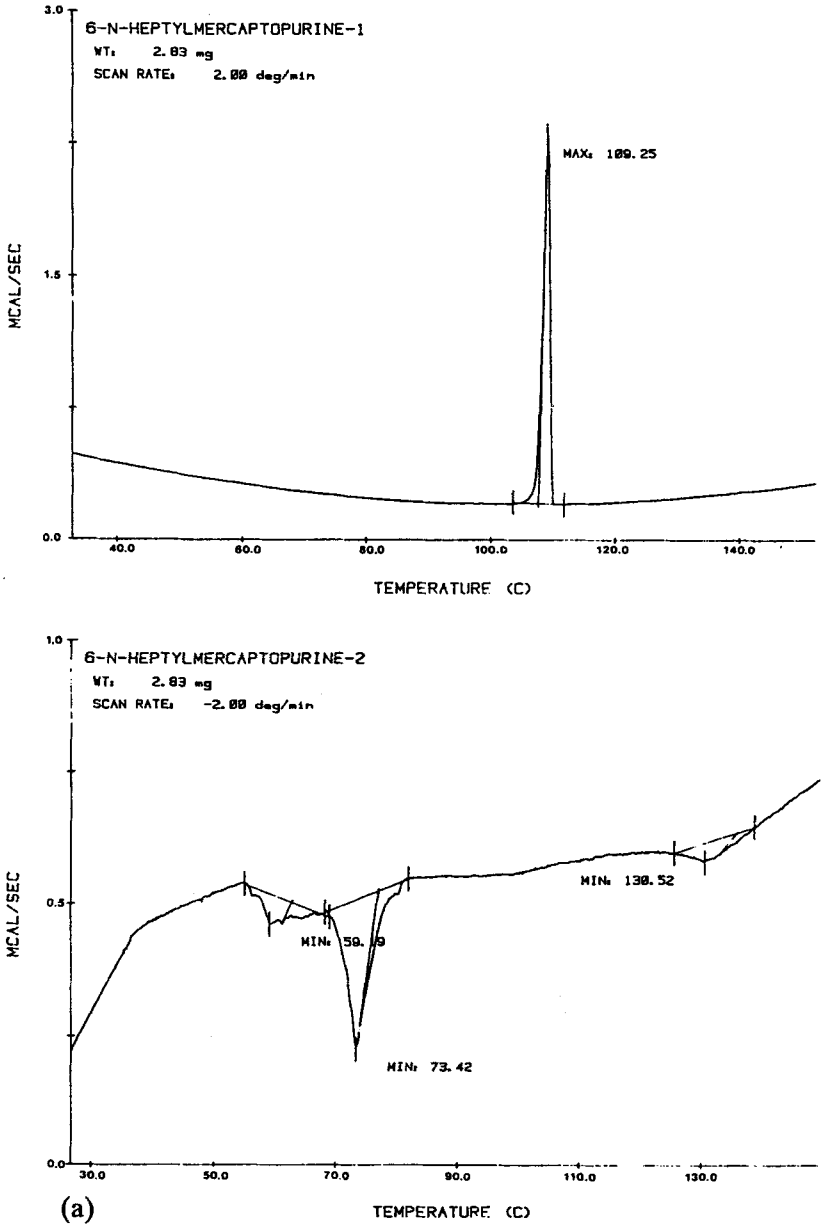
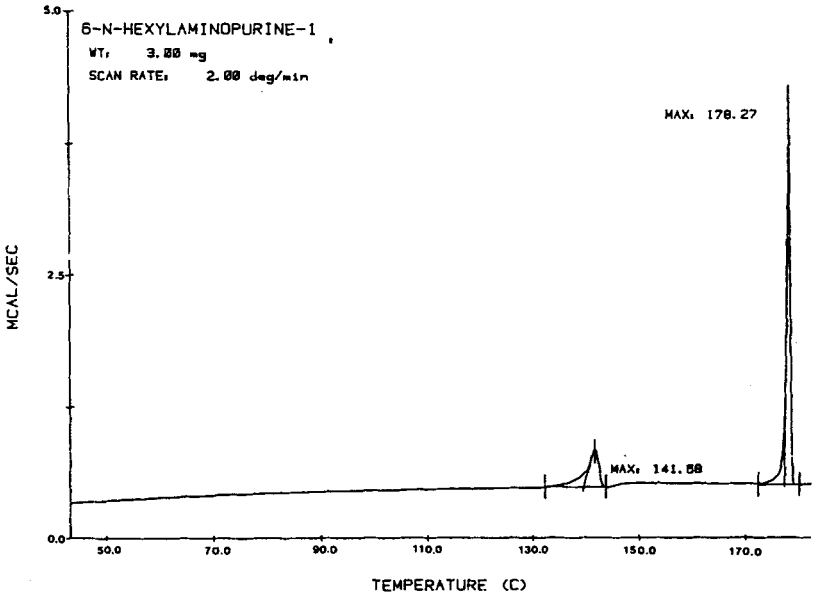
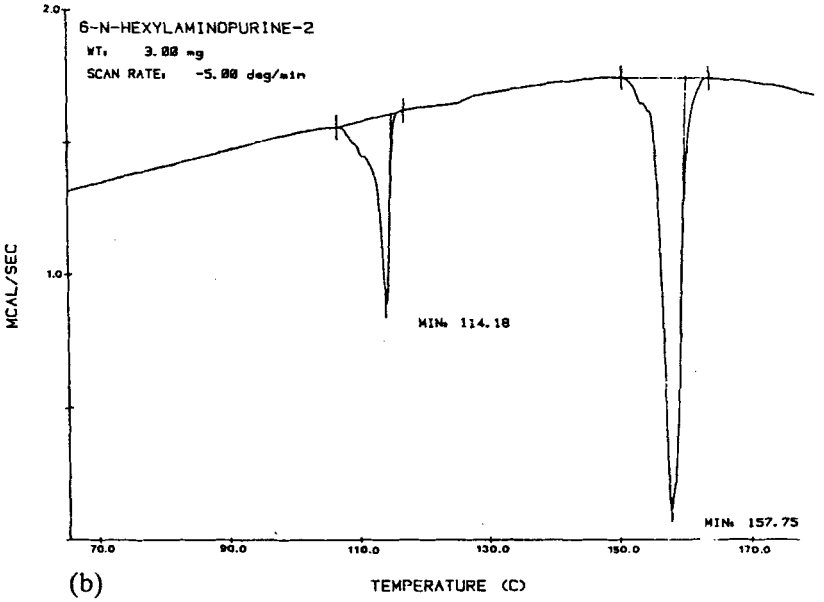



FIGURE 1 Differential scanning calorimeter thermograms of
(a) 6-N-heptylmercaptopurine,
(b) 6-N-hexylaminopurine
1—heating cycle; 2—cooling cycle.

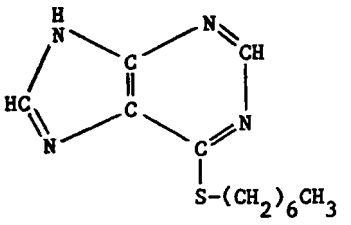


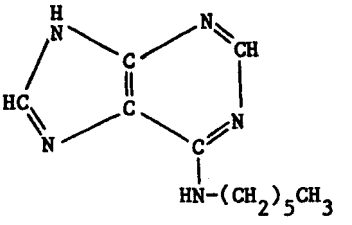

(b)

FIGURE 1 (Continued)

shows no phase transitions on the heating cycle and a complex transition at 59 to 73°C which is probably a supercooling effect. Neither compound forms a thermotropic liquid crystal.




(I)




(II)

Their crystal structure analyses were therefore determined to seek information concerning the molecular packing and intermolecular forces in the crystalline state, which might have bearing on the comparison with the structures of related mesogenic amphiphiles such as the alkyl glycosides[2] and alkoxy benzoic acids.[3]

## EXPERIMENTAL

Crystals of I suitable for X-ray structure analysis, were obtained from the Sigma Chemical Company without recrystallization. Crystals of II were obtained by recrystallization of a sample from the same source, using a methanol, ethanol, 2-propanol, water mixture. The experimental data are given in Table I. Both structures were solved by MITHRIL.[4] E-maps revealed all non-hydrogen atoms of both structures. In I, all the hydrogen atoms except four, H(11′), H(12), H(12′), H(13′) of the alkyl chain, were located on difference synthesis. These atoms were placed in calculated positions, which were refined with those observed using isotropic temperature factors.

In II, eleven of the seventeen hydrogen atoms were located directly, the remainder were placed in calculated positions. The hydrogen atom parameters were included in the calculations, but not refined.

The structure refinement data are included in Table I. The crystals of I were more suitable than those of II for an accurate analysis, which was carried out at 123 K. The atomic parameters are reported in Table II,† corresponding to the atomic notation shown in Figures 2(a) and (b), which also shows the thermal ellipsoids.

†Tables of anisotropic temperature parameters for I and II, H-atom positional parameters for II, and lists of torsion angles, selected least-squares planes, and observed and calculated structure factors for I and II have been provided to the editor and are available upon request from the authors.

TABLE I

Crystal structure, experimental, and refinement data for 6-N-heptylmercaptopurine, I, at 123 K and for 6-N-hexylaminopurine, II, at room temperature

| | I | II |
|---|---|---|
| Formula | $C_{12}H_{18}N_4S$ | $C_{11}H_{17}N_5$ |
| Space group | $P2_1/c$, Z = 4 | $P\bar{1}$, Z = 2 |
| Cell dimensions | at 123 K [295 K] based on 21 reflections with $17° < \theta < 22°$ | at 295 K based on 38 reflections with $10° < \theta < 14°$ |
| a (Å) | 15.527(7) [15.219(7)] | 5.214(10) |
| b (Å) | 7.140(3) [ 7.275(3)] | 8.466(13) |
| c (Å) | 11.979(6) [12.414(7)] | 13.932(40) |
| α (°) | 90.0 | 97.03(16) |
| β (°) | 101.21(4) [100.15(4)] | 92.03(17) |
| γ (°) | 90.0 | 104.43(17) |
| V (Å$^3$) | 1302.69 [1352.94] | 589.71 |
| $D_x$ (g/cm$^3$) | 1.276 [1.228] | 1.212 |
| $D_m$ (g/cm$^3$) | 1.247 | 1.228 |
| m.p. (°C) | 110.0 | 179.5 |
| Crystal dimensions (mm) | 0.13 × 0.3 × 0.7 | 0.04 × 0.26 × 0.5 |
| Radiation | MoKα (λ = 0.7107 Å), Nb filter | |
| $\mu_{MoK\alpha}$(cm$^{-1}$) | 2.3 | 0.85 |
| Diffractometer & method | CAD-4, ω/2θ scan | |
| No. reflections measured | 3758 | 1080 |
| No. reflections observed | 2424, I > 2 σ(I) | 620, I > 1 σ(I) |
| $\theta_{max}$ (°) | 30 | 20 |
| Range of h,k,l: h | −21, +21 | 0, 5 |
| k | 0, 10 | −8, 8 |
| l | 0, 16 | −13,13 |
| Function minimized | $R = \Sigma[\omega(k\|F_o\| - \|F_c\|)^2]$, using program UPALS (ref. 5), $\omega = 1/\sigma^2(F)$ based on counting statistics | |
| Final electron density (e/Å$^3$) on difference Fourier map | 0.45 | 0.25 |
| Final agreement $R(F)$ | 0.049 | 0.078 |
| $R_w(F)$ | 0.045 | 0.057 |
| $S$ | 1.41 | 1.39 |

## RESULTS

### The Molecular Packing and Hydrogen Bonding

The packing of the molecules in the crystals is shown in Figures 3 and 4. That in compound I is isostructural with those of the alkyl glucosides having alkyl chain lengths greater than six carbon atoms. The purine moieties, related by a center of symmetry, form planes of hydrogen-bonded dimers with interdigitated side chains (Figure 3a). The dimers, related by two-fold screw axis, pack in a herring-bone pattern with an angle between the mean plane of the purine

TABLE II

Atomic parameters for N-heptylmercaptopurine, I, at 123 K and N-hexylaminopurine, II, at 295 K

| Atom | x/a | y/b | z/c | $B_{eq}$ or $B_{iso}$ |
|---|---|---|---|---|
| | | Compound I | | |
| S | 6920.9(4) | 2355.2(9) | 5931.8(5) | 1.47(1) |
| N(1) | 6777(1) | −620(3) | 4516(2) | 1.39(5) |
| N(3) | 5859(1) | −3332(3) | 4586(2) | 1.27(4) |
| N(7) | 5502(1) | −285(3) | 6828(2) | 1.28(4) |
| N(9) | 5018(1) | −3090(3) | 6108(2) | 1.30(5) |
| C(2) | 6436(1) | −2291(3) | 4163(2) | 1.44(5) |
| C(4) | 5611(1) | −2500(3) | 5477(2) | 1.10(4) |
| C(5) | 5910(1) | −757(3) | 5934(2) | 1.09(5) |
| C(6) | 6520(1) | 175(3) | 5415(2) | 1.17(5) |
| C(8) | 4981(2) | −1713(3) | 6886(2) | 1.37(5) |
| C(11) | 7500(2) | 3129(4) | 4836(2) | 1.59(6) |
| C(12) | 8418(2) | 2322(4) | 4922(2) | 1.65(5) |
| C(13) | 8902(2) | 3204(4) | 4058(2) | 1.71(6) |
| C(14) | 9819(2) | 2383(4) | 4129(2) | 1.72(5) |
| C(15) | 10339(2) | 3256(4) | 3302(2) | 1.68(6) |
| C(16) | 11267(2) | 2478(4) | 3432(2) | 2.01(6) |
| C(17) | 11803(2) | 3374(5) | 2636(3) | 2.58(8) |
| H(2) | 663(1) | −282(3) | 355(2) | 0.7(4) |
| H(8) | 537(1) | 320(3) | −238(2) | 0.7(5) |
| H(9) | 530(2) | 90(4) | −99(2) | 2.6(2) |
| H(11) | 715(2) | 287(4) | 412(2) | 2.8(7) |
| H(11′) | 248(2) | 554(4) | 507(2) | 2.1(6) |
| H(12) | 836(2) | 95(4) | 478(2) | 1.6(5) |
| H(12′) | 878(2) | 254(4) | 571(2) | 2.1(5) |
| H(13) | 103(2) | −41(4) | 80(3) | 3.0(7) |
| H(13′) | 855(2) | 305(4) | 330(2) | 2.3(6) |
| H(14) | 1015(2) | 254(4) | 488(2) | 2.8(6) |
| H(14′) | 975(2) | 101(4) | 397(2) | 2.1(6) |
| H(15) | 1003(2) | 305(3) | 254(2) | 1.7(5) |
| H(15′) | 1037(2) | 465(4) | 344(2) | 2.0(6) |
| H(16) | 1124(2) | 113(4) | 335(2) | 2.1(6) |
| H(16′) | 1161(2) | 261(4) | 426(2) | 2.9(6) |
| H(17) | 1239(2) | 289(4) | 283(2) | 2.1(6) |
| H(17′) | 1185(2) | 476(4) | 275(2) | 2.7(7) |
| H(17″) | 1155(2) | 320(5) | 185(3) | 4.5(9) |
| | | Compound II | | |
| Atom | x/a | y/b | z/c | $B_{eq}$ |
| N(1) | 394(2) | 401(1) | 199.6(6) | 3.7(3) |
| N(3) | 768(2) | 490(1) | 103.8(7) | 4.0(3) |
| N(6) | 50(2) | 165.3(9) | 150.0(6) | 3.5(3) |
| N(7) | 341(2) | 133.9(9) | −37.6(7) | 3.6(3) |
| N(9) | 733(1) | 313(1) | −48.9(7) | 3.9(3) |
| C(2) | 621(2) | 499(1) | 179.1(8) | 3.9(4) |
| C(4) | 642(2) | 359(1) | 38.2(9) | 3.5(4) |
| C(5) | 400(2) | 248(1) | 43.6(8) | 3.0(4) |
| C(6) | 277(2) | 269(1) | 130.1(8) | 2.9(4) |
| C(8) | 541(2) | 176(1) | −92.8(7) | 4.1(4) |

TABLE II

(Continued)

| Atom | x/a | Compound II y/b | z/c | $B_{eq}$ |
|---|---|---|---|---|
| C(11) | −68(2) | 188(1) | 242.9(8) | 4.1(4) |
| C(12) | 68(2) | 128(1) | 325.0(7) | 4.5(4) |
| C(13) | 33(2) | −57(1) | 313.4(7) | 4.8(4) |
| C(14) | 204(2) | −112(1) | 385.7(8) | 5.4(4) |
| C(15) | 173(2) | −294(1) | 376.5(8) | 6.1(5) |
| C(16) | 340(3) | −351(1) | 488.1(9) | 8.1(6) |

Non-hydrogen atom positional parameters are x $10^4$ for I, x $10^3$ for II. Hydrogen atom positional parameters are x $10^3$ for I; those for II have been provided to the Editor and are available upon request from the authors. $B_{eq} = 4/3\Sigma_i\Sigma_j\beta_{ij}(a_i \cdot a_j)$.

rings of 54°. The chain is in an all-extended form and is *trans* with respect to the purine moiety. The adjacent purine rings are stacked in pairs, with separations of 3.43 Å between the mean planes of the ring. Superpositions of the pairs of stacked purine rings are shown in Figure 5a. The shortest intermolecular distances are N(1)—C(8) = 3.355 Å, N(9)—C(6) = 3.417 Å, C(5)—C(5) = 3.423 Å, and C(6)—C(8) = 3.426 Å.

In II, the purine rings form infinite hydrogen-bonded layers, which propagate in the *a* direction (Figure 4a), with parallel stacking as shown in Figure 4b. The alkyl chains are not intercalated. The least-squares plane formed by C(11), C(12), C(13), C(14), C(15), C(16) makes an angle of −82° with the least-squares purine plane. The stacking pattern is quite different from I, as shown in Figure 5b. The N(9) and N(3) atoms are positioned approximately above the centers of 6- and 5-membered rings, respectively, and the interplanar spacing between purine moieties, related by $x, y, z \rightarrow 1 - x, 1 - y, -z$, is 3.49 Å. The shortest intermolecular distances are N(9)—C(2) = 3.343 Å, C(4)—C(4) = 3.367 Å, C(2)—C(8) = 3.408 Å, N(3)—C(4) = 3.435 Å, N(3)—C(5) = 3.445 Å.

Compound I has one hydrogen-bond donor group, N(9)H, and three hydrogen-bond acceptors N(1), N(3), and N(7). Only one hydrogen bond is formed, N(9)H—N(3), with H—N(3) = 2.08(3) Å, N(9)—H = 0.87(3) Å and an N(9)—H—N(3) angle of 165(3)°. This bond links molecules related by symmetry operation $x, y, z \rightarrow 1 - x, 1 - y, 1 - z$. Compound II has two hydrogen-bond donor groups N(6)—H, N(9)—H and three acceptors N(1), N(3), N(7). Two hydrogen bonds are formed. One is N(6)—H—N(7) [N(6)—H = 1.06 Å, H—N(7) = 2.02 Å, N(6)—H—N(7) = 159°]. This corresponds

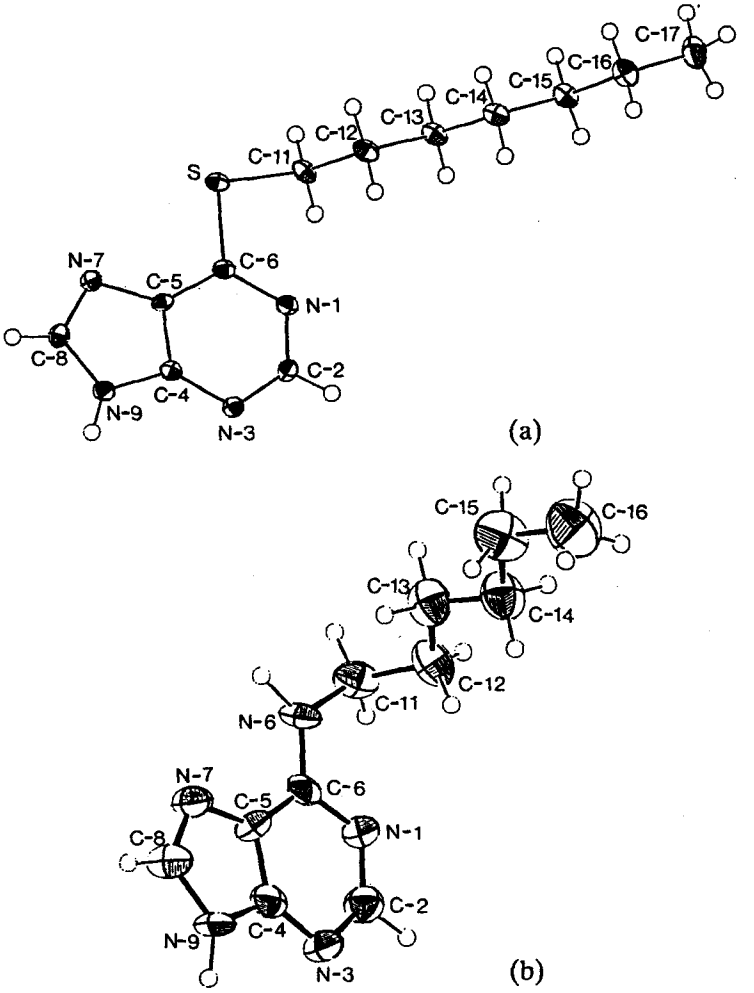



FIGURE 2 ORTEP drawing with atomic notation for
(a) 6-N-heptylmercaptopurine, (123 k).
(b) 6-N-hexylaminopurine (295 k).
(50 percent probabilities)

to that in the type II base-pairing of the 28 different types of base-base interactions formed in crystal structures of individual bases, nucleosides and nucleotides.[6] The other hydrogen bond, N(9)—H—N(3), with N(9)—H = 1.06Å, H—N(3) = 1.86 Å and N(9)—H—N(3) = 167°, is similar to that observed in I.

It is tempting to speculate on the relationship between these crystal structures and those of the alkyl glycosides, and the observation that

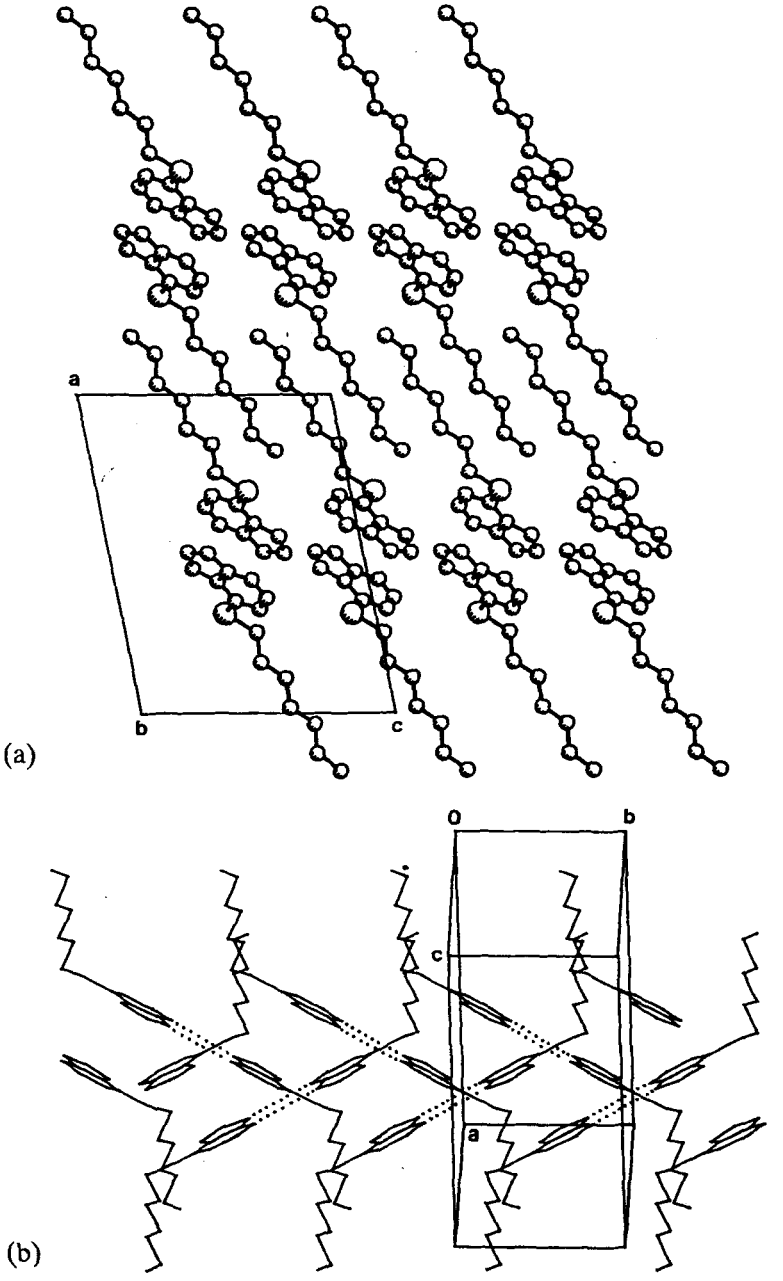



FIGURE 3 The molecular packing in 6-N-heptylmercaptopurine, I.
(a) view along the *b* axis,
(b) the herring-bone type of packing.

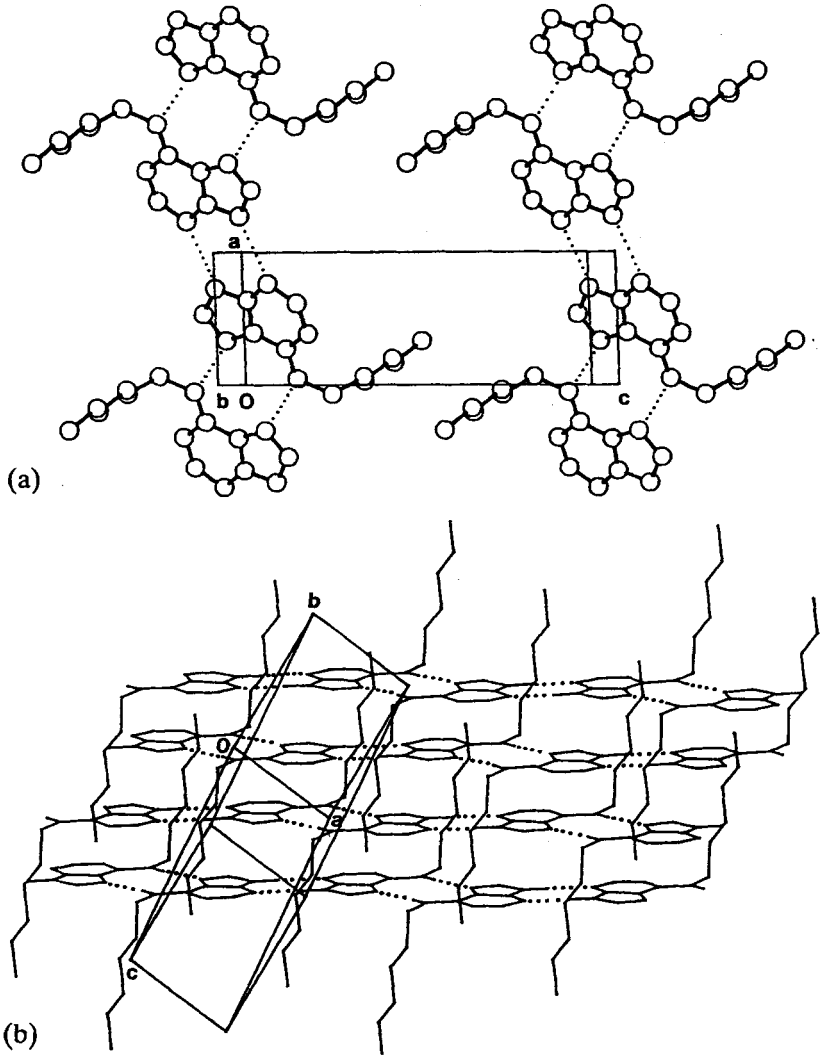



FIGURE 4 The molecular packing in 6-N-hexylaminopurine, II.
(a) view along the *b* axis,
(b) imbricated stacking of hydrogen-bonded purine moieties.

these amphiphilic molecules do not form mesophases. In I, the cohesive forces between the purine moieties, i.e., the hydrogen bonding and stacking forces, which would form the *core* of the liquid crystal cluster, are weaker than in either the alkyl glucosides or the alkoxy benzoic acids. Furthermore, the molecular length to breadth ratio is

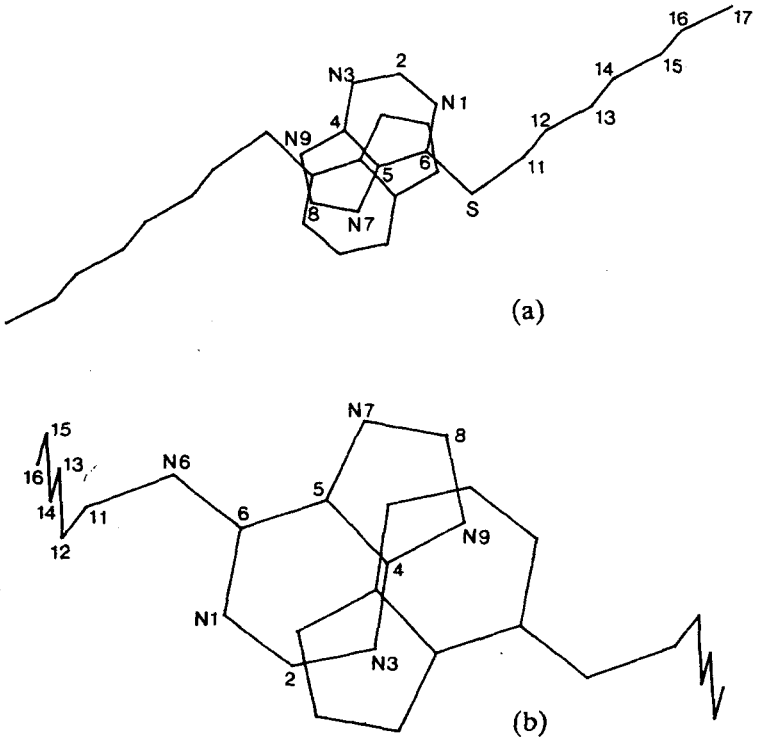



FIGURE 5 Overlapping regions of the purine moieties in
(a) 6-N-heptylmercaptopurine, I,
(b) 6-N-hexylaminopurine, II.

less favorable. It is possible that molecules with longer alkyl chains would have the same type of molecular packing in the crystal and have thermotropic liquid crystal phases. For either, or both, of these reasons, the molecular clusters would be less stable with respect to thermal motion at the temperature between the highest crystal phase and the melting point at 109°C. That is to say that the cohesion between the hydrophilic component of the molecules is insufficient to sustain the core of the liquid crystal cluster above the highest crystal transition.

In II, in contrast, the crystal structure suggests that it is the non-polar, hydrophobic, component which is deficient as a mesophase. The crystal structure is determined primarily by the combination of hydrogen-bonding of the base-pair type, plus strong van der Waals stacking forces. This strong core structure persists over sufficient temperature range that the thermal motion disrupts the whole struc-

ture completely at the melting point of 179.5°C, which is significantly higher than that of I.

### The Molecular Structures

The bond distances and valence angles of both structures are given in Table III. The molecular dimensions of the purine moieties agree with the average values of twenty-one 9-substituted adenine structures.[7] The 6-N-hexylaminopurine structure has been determined with low accuracy due to the poor quality of the crystal under study.

In I, there is a significant difference (0.07 Å, ~27) between C(6)—S [1.744(2) Å] and S—C(11) [1.814(3)Å], indicating a partial double bond character for the C(6)—S bond. A similar shortening is observed in II; C(6)—N(6) = 1.35(1) Å compared with N(6)—C(11) = 1.46(1) Å (Table III). The mean aliphatic C—C bond lengths are 1.525(3) Å and 1.51(1) Å in I and II respectively and the mean C—C—C valence angles are 113.1(1.0) and 114.8(9)°.

The purine moiety of I is significantly non-planar. The $\chi^2$ value obtained from the least squares plane calculations is 252.4. The maximum deviations are observed for the C(4) (8σ) and C(5) (~10σ) atoms. The sulfur atom lies in the least squares plane, with a distance from the plane of 0.006(2) Å. In II, the purine is planar within the low accuracy of the atomic positions, $\chi^2 = 15.9$.

Both alkyl chains are in the *trans* position with respect to the purine moieties. The torsion angles C(5)—C(6)—S(1)—C(11) in I and C(5)—C(6)—N(6)—C(11) in II are −169.7(2)° and 178(1)°, respectively. The heptyl chain is in an all-extended form and the angle between the chain plane through C(11), C(12), C(13), C(14), C(15), C(16), C(17) and the purine plane is 75°. In II, the hexyl chain is twisted around the C(11)—C(12) bond; the corresponding torsion angle N(6)—C(11)—C(12)—C(13) is −67(1)°. The least-squares plane of the carbon chain makes an angle of −82° with the purine plane. The sulfur atom is 0.247(3) Å from the heptyl chain plane in I, and N(6) is at 1.39(2) Å in II.

TABLE III

Bond distances and bond angles with their e.s.d.'s for 6-N-heptylmercaptopurine, I, at 123 K, and 6-N-hexylaminopurine, II, at 295 K

| Bond | I (Å) | II (Å) |
|---|---|---|
| N(1)—C(2) | 1.340(3) | 1.33(1) |
| C(2)—N(3) | 1.337(3) | 1.33(1) |
| N(3)—C(4) | 1.342(3) | 1.36(1) |
| C(4)—C(5) | 1.402(3) | 1.38(1) |

TABLE III

(Continued)

| Bond | I (Å) | II (Å) |
|---|---|---|
| C(5)—C(6) | 1.399(3) | 1.40(1) |
| C(6)—N(1) | 1.344(3) | 1.38(1) |
| C(5)—N(7) | 1.388(3) | 1.36(1) |
| N(7)—C(8) | 1.313(3) | 1.32(1) |
| C(8)—N(9) | 1.363(3) | 1.39(1) |
| N(9)—C(4) | 1.366(3) | 1.36(1) |
| C(6)—S | 1.744(2) | — |
| S—C(11) | 1.815(3) | — |
| C(6)—N(6) | — | 1.35(1) |
| N(6)—C(11) | — | 1.46(1) |
| C(11)—C(12) | 1.523(4) | 1.52(1) |
| C(12)—C(13) | 1.528(4) | 1.52(1) |
| C(13)—C(14) | 1.527(4) | 1.51(1) |
| C(14)—C(15) | 1.528(4) | 1.50(1) |
| C(15)—C(16) | 1.524(4) | 1.50(1) |
| C(16)—C(17) | 1.522(4) | — |
| **Angle** | **I (deg)** | **II (deg)** |
| C(6)—N(1)—C(2) | 117.9(2) | 116.6(9) |
| N(1)—C(2)—N(3) | 128.9(2) | 131.3(9) |
| C(2)—N(3)—C(4) | 111.8(2) | 109.1(9) |
| N(3)—C(4)—C(5) | 125.4(2) | 128(1) |
| N(3)—C(4)—N(9) | 129.2(2) | 125(1) |
| C(5)—C(4)—N(9) | 105.4(2) | 106(1) |
| C(4)—C(5)—C(6) | 116.8(2) | 115(1) |
| C(4)—C(5)—N(7) | 110.5(2) | 111(1) |
| C(6)—C(5)—N(7) | 132.7(2) | 134(1) |
| C(5)—C(6)—N(1) | 119.1(2) | 119(1) |
| C(5)—N(7)—C(8) | 103.3(2) | 105.2(8) |
| N(7)—C(8)—N(9) | 114.6(2) | 111.9(9) |
| C(8)—N(9)—C(4) | 106.1(2) | 106.0(9) |
| N(1)—C(6)—S | 121.4(2) | — |
| C(5)—C(6)—S | 119.5(2) | — |
| C(6)—S—C(11) | 102.0(1) | — |
| N(1)—C(6)—N(6) | — | 118(1) |
| C(5)—C(6)—N(6) | — | 126(1) |
| C(6)—N(6)—C(11) | — | 121.6(8) |
| S—C(11)—C(12) | 115.1(2) | — |
| N(6)—C(11)—C(12) | — | 113.3(8) |
| C(11)—C(12)—C(13) | 112.0(2) | 114.3(8) |
| C(12)—C(13)—C(14) | 112.3(2) | 113.9(9) |
| C(13)—C(14)—C(15) | 114.3(2) | 115.2(9) |
| C(14)—C(15)—C(16) | 113.1(2) | 116(1) |
| C(15)—C(16)—C(17) | 113.8(2) | — |

### The Thermal Motion Analysis

A thermal motion analysis was carried out for I, but not for II because of the poor quality of the room temperature data set. For I, the $\Delta(A,B) = \langle U_A^2 \rangle - \langle U_B^2 \rangle$, where $\langle U_A^2 \rangle$ and $\langle U_B^2 \rangle$ are mean-square amplitudes of thermal vibration for atoms $A$ and $B$ along the interatomic vectors A—B within the molecule, were calculated[7] to test the non-rigid motion. The largest $\Delta(A,B)$ values were found for S(1)—C(8), 0.006(1) Å$^2$, and between atoms in the purine molecule and two terminal atoms from the side chain, C(16) and C(17), with $\Delta(A,B)$ ranging from 0.005(2) to 0.0080(16) Å$^2$. These differences are about 3 times smaller than those in the crystal structure of heptyl 1-thio-α-D-manndipyranoside,[8,9] indicating more rigid-bond thermal motion in 6-N-heptylmercaptopurine. Analysis of the molecular vibrations, assuming a simple rigid-body model, gave $R_w = [w_k\Delta_k^2/\Sigma w_k(U_{ij})_o^2]^{1/2} = 0.125$ and $s = [\Sigma w_k\Delta_k^2/(n - m)]^{1/2} = 2.28$, where $n = 102$ is the number of observations, and $m = 20$ is the number of variables, using a computer program by Craven & He.[10] The largest $\Delta U_{ij}/\sigma$ were found for C(16) and C(17), $U_{11} = 4.1$ Å$^2$ and $U_{22} = 6.4$ Å$^2$ respectively. A model assuming two rigid molecular fragments (the purine moiety and the side chain) and introducing the internal libration axis along the C(6)—S(1) bond, or along any other bond within a side chain, gave no significant improvement over the simple rigid body model. On the other hand, a rigid body model is oversimplified by the assumption that molecules vibrate independently, when in fact they are coupled by H-bonding and other interactions in crystal structures. The corrections for bond lengths obtained from the rigid-body model were insigificant ($< 1\sigma$).

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### Supplementary Material Available

Tables may be obtained by contacting Gordon and Breach, 50 West 23rd St., New York, NY 10010.

## References


1. G. A. Jeffrey, *Mol. Cryst. Liq. Cryst.*, **110**, 221–237 (1984).
2. G. A. Jeffrey, *Accts. Chem. Res.*, **19**, 168–173 (1986).
3. R. F. Bryan, P. Hartley, R. W. Miller, and M.-S. Shen, *Mol. Cryst. Liq. Cryst.*, **62**, 281–310 (1980).
4. C. J. Gilmore, *MITHRIL, A Computer Program for the Automatic Solution of Crystal Structures from X-ray Data* (Department of Chemistry, University of Glasgow, Scotland, 1983).
5. J. O. Lundgren, *UPALS—A Full-Matrix Least-Squares Refinement Program* (Institute of Chemistry, University of Uppsala, Sweden, 1978).
6. W. Saenger, *Principles of Nucleic Acid Structure* (Springer-Verlag, 1984), p. 120.
7. R. Taylor and O. Kennard, *J. Mol. Struct.*, **78**, 1–28 (1982).
8. D. C. Carter, J. R. Ruble, and G. A. Jeffrey, *Carbohydr. Res.*, **102**, 59–67 (1982).
9. X. M. He and B. M. Craven, *Acta Crystallogr., Sect. A*, **41**, 244–251 (1985).
10. B. M. Craven and X. M. He, *Programs for Thermal Motion Analysis* (Department of Crystallography, University of Pittsburgh, 1982).