

Supramolecular Structures formed from Hydrogen-bonded Networks of 5-Alkoxyisophthalic Acid

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A molecular model based on 5-alkoxyisophthalic acid and bifunctional aromatic bases for developing supramolecular structures is described; the molecular self-assembly of the title compounds in the crystal lattice and its modification with added diamines is characterised by single crystal analyses.

The self-organisation of molecules to form well-defined supramolecular structures under the influence of weak forces such as hydrogen bonds, electrostatic interactions and hydrophobic effects has been explored extensively in solution,¹ in monolayers,² and in the solid state.^{3,4} While low-molecular mass liquid crystalline materials have been obtained,^{5,6} there are only a few studies extending this concept to generate a polymeric hydrogen-bonded network with a stable mesophase.^{7,8} We decided to combine the directionality of the hydrogen bonding and the hydrophobic interaction of alkyl chains within a single molecule and to explore the interplay of these forces in the formation of both mesophases and solid lattices. Our model system is based on monoalkyl derivatives of 5-hydroxyisophthalic acid **1** (C_n ISA) and bifunctional aromatic bases with two basic nitrogen atoms such as pyridazine, pyrimidine, pyrazine and bipyridine (Scheme 1).

The isophthalic acid derivatives were prepared from the commercially available dimethyl 5-hydroxyisophthalate by known procedures for the alkylation of phenols with different alkyl bromides followed by the hydrolysis of the ester groups.[†]

The crystal structures of alkoxy substituted isophthalic acids with pyrazine, pyrimidine and ethanol are shown in Figs. 1–3.‡ In the structure of C_{12} ISA·½ pyrazine the diacid molecules form chains through hydrogen bonding between one of their –OH groups and a O=C group of the neighbouring molecule. These chains are cross-linked thereby forming molecular ribbons *via* hydrogen bonding between the remaining –OH group and the nitrogen atom of the pyrazine ring. As the alkyl side chains of two neighbouring ribbons interdigitate, a double layer structure is formed with a head-head-tail-tail arrangement of the acid molecules. The C_{12} ISA molecule is almost planar; only one of the two –CO₂H groups is slightly rotated out of the molecular plane. The layers are stacked in a staggered fashion, *i.e.* the next sheet is shifted by about half the thickness of the hydrogen-bonded double strand in the side-chain direction. Thus only about half the atoms in the side chains are involved in three-dimensional alkyl group packing (Fig. 1).

The crystal structure of C_{16} ISA·pyrimidine shows a similar head-head-tail-tail arrangement of planar molecules (Fig. 2). Here a zig-zag chain of alternating pyrimidine rings and isophthalic acid molecules is formed by O–H...N hydrogen bonds and molecular ribbons, with only weak interactions between the adjacent ribbons being found.

If C_{12} ISA is crystallised from ethanol, crystals of the ethanol solvate are obtained. The crystal structure is shown in Fig. 3. Ethanol acts as hydrogen-bond donor and acceptor. One molecule of ethanol is inserted into the hydrogen-bonded

chain of the acid groups. The resulting structure is a ribbon similar to C_{16} ISA·pyrimidine. Here the ribbons are not flat, but an angle of *ca.* 35° between the hydrogen-bonded chain and the layer of alkyl groups is observed [Fig. 3(b)].

In all three structures alkyl chains of different layers take part in a three-dimensional close packing. Identical subcells of the alkyl groups are found in all structures with only small deviations. They are all monoclinic, $a = 4.2(1)$, $b = 4.4(1)$, $c = 2.54(3)$ Å, $\gamma = 115(5)^\circ$, with the setting angle of the chains on a being $115(5)^\circ$. This is one of the stable forms for the packing of polymethylene chains predicted by Kitaigorodskii.⁹ The observation that in all cases studied the alkyl side groups are in an all-*trans* conformation and pack in an infinite array with an energetically favoured subcell vindicates the concept that in the cases investigated alkyl group interaction plays an active part in the development of supramolecular architectures.

The nature of the interaction between the components was also established by IR spectroscopy¹⁰ and seen as hydrogen bonding between the diacids and the aromatic diamines. The peak at 1686 cm^{-1} in the IR spectrum of pure diacid indicates dimer formation in the pure material. The strong absorption at 1708 cm^{-1} (free C=O) and O–H peak at 2506 cm^{-1} in case of

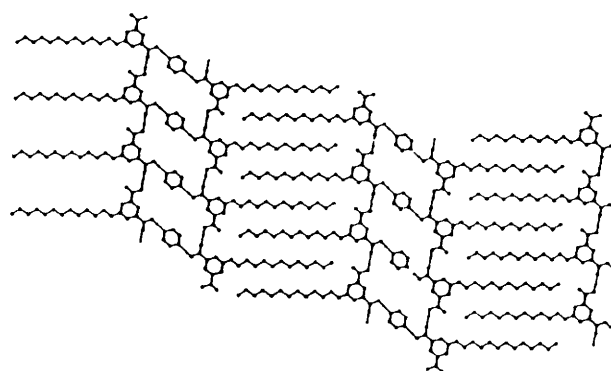


Fig. 1 Crystal structure of C_{12} ISA·½pyrazine. Projection on the molecular sheet.

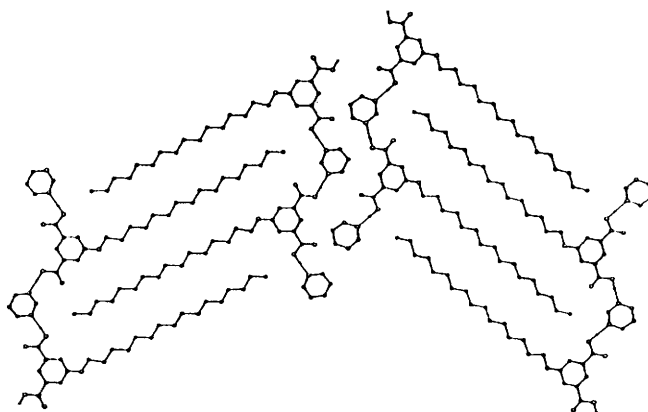
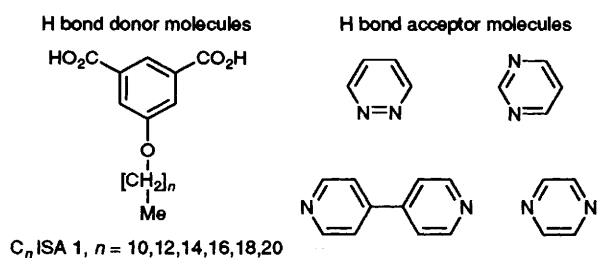


Fig. 2 Crystal structure of C_{16} ISA·pyrimidine. Projection on the molecular sheet.



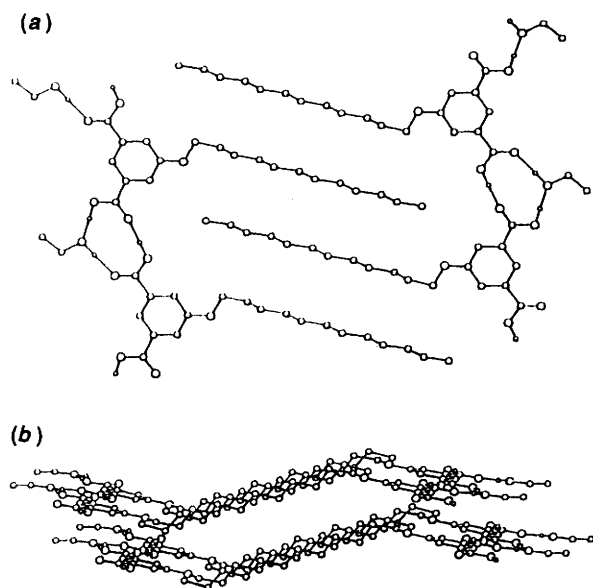


Fig. 3 Crystal structure of $C_{12}ISA \cdot EtOH$. (a) Projection on the molecular sheet; (b) projection perpendicular to the hydrogen-bonded sheets.

the mixture of diacid and bipyridine and all aromatic amines clearly indicate that hydrogen bonding between the acid groups and the nitrogen atoms of the diamine is the major interaction which cause the self-organisation of the molecules in the solid lattice and in the mesophase. The absence of strong absorption around 1720 cm^{-1} in all cases indicates the presence of only hydrogen-bonded acid molecules at room temperature.

In a complementary approach the dicarboxylic acids and their mixtures with diamines (1:1 molar ratio) were studied for their possible liquid crystalline properties. All dicarboxylic acids are thermally stable under nitrogen during repeated DSC scans and X-ray measurements. The pure acids and the mixtures show distinctive thermotropic behaviour.

Studies of the thermal behaviour of these compounds using an optical polarizing microscope show characteristic changes in textures with phase transitions observed in the thermogram. Mixtures of the diacids and diamines exhibit different textures from that of pure diacids under a polarised beam of light. These factors in combination with the DSC and single-crystal analyses indicate that the molecular organisation in the mixture of a diacid and a diamine is different from that of the pure diacids. The results of these studies will be published elsewhere.

In conclusion, we report on a molecular model for creating polymeric networks, whose supramolecular organisation rests upon an interplay of hydrogen bonding patterns and side-chain packing. In contrast to other systems²⁻⁸ ours possesses important advantages such as simple synthesis of the complementary monomer molecules and easy structural characterisation of the polymeric network. Furthermore, no preorganisation of hydrogen-bond donor and acceptor sites is required.[¶]

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Footnotes

† All compounds were characterised by spectroscopic methods and show the satisfactory elemental analyses. The mixtures were prepared by the accurate weighing of the diacid and the diamine in a 1:1 stoichiometry and by dissolving the mixtures in tetrahydrofuran to obtain a homogeneous solution. Slow evaporation of the solvent at

room temperature yielded a solid residue which was further dried under high vacuum.

‡ Single crystals suitable for X-ray crystal structure analyses were grown by slow evaporation of THF solutions for $C_{12}ISA \cdot 1/2$ pyrazine and $C_{16}ISA \cdot$ pyrimidine and from ethanol for $C_{12}ISA \cdot EtOH$. *Crystal data*: Enraf-Nonius CAD4 diffractometer, graphite-monochromated Cu-K α radiation ($\lambda = 1.5405\text{ \AA}$). The structures were solved by direct methods and refined by full-matrix least squares analyses with anisotropic thermal parameters for C, N, O. The H atoms were refined in the riding mode with fixed isotropic thermal parameters. Programs used: SIR88, Molen.

$C_{12}ISA \cdot 1/2$ pyrazine: $a = 9.0006(7)$, $b = 8.7349(8)$, $c = 14.637(1)\text{ \AA}$, $\alpha = 81.697(8)^\circ$, $\beta = 94.146(7)^\circ$, $\gamma = 73.324(7)^\circ$, $V = 1083\text{ \AA}^3$, $P1$, $Z = 2$, $D_c = 1.198\text{ g cm}^{-3}$, $\mu = 6.47\text{ cm}^{-1}$; 3014 measured reflections of which 2274 were observed [$I > 3\sigma(I)$], $R = 0.066$, $R_w = 0.064$. $C_{16}ISA \cdot$ pyrimidine at 225 K: $a = 10.9527(10)$, $b = 60.685(10)$, $c = 4.1013(7)\text{ \AA}$, $\beta = 96.259(11)^\circ$, $V = 2710\text{ \AA}^3$, $P2_1/n$, $Z = 4$, $D_c = 1.193\text{ g cm}^{-3}$, $\mu = 6.17\text{ cm}^{-1}$; 3841 measured reflections of which 2057 were observed [$I > 3\sigma(I)$], $R = 0.044$, $R_w = 0.047$. $C_{12}ISA \cdot EtOH$: $a = 5.4999(9)$, $b = 7.8139(6)$, $c = 53.301(4)\text{ \AA}$, $\beta = 91.483(10)^\circ$, $V = 2290\text{ \AA}^3$, $P2_1/c$, $Z = 4$, $D_c = 1.278\text{ g cm}^{-3}$, $\mu = 7.16\text{ cm}^{-1}$; 3135 measured reflections of which 1981 were observed [$I > 3\sigma(I)$], $r = 0.062$, $R_w = 0.078$. Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen on quoting the depository number, the names of the authors and the journal citation. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ IR spectra were recorded on a Nicolet FT-IR spectrometer using KBr pellets. Variable temperature IR measurements are currently in progress and the results will be reported later.

¶ Added in proof: Pure C_nISA with a shorter alkyl chain has recently been shown to form cyclic hexameric aggregates.¹¹

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