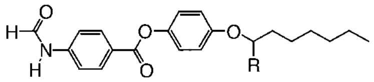
Homo- and Heterochiral Supramolecular Tapes from Achiral, Enantiopure, and Racemic Promesogenic Formamides: Expression of Molecular Chirality in Two and Three Dimensions**

Steven De Feyter, André Gesquière, Klaus Wurst,
David B. Amabilino, Jaume Veciana,* and
Frans C. De Schryver*

Understanding how a stereogenic center influences conformations at the molecular scale and organization at the supramolecular level is an elusive and intriguing challenge in a number of scientific disciplines.[1] A very interesting challenge is to prepare self-assembling systems and to study how the chiral nature of the component compounds in combination with the self-assembly process affects the ordering in two and three dimensions. In both two- and three-dimensional (2D and 3D, respectively) systems, pure enantiomers form enantiomorphous structures.

But what happens when equimolar mixtures of enantiomers are crystallized or are physisorbed at a surface? Will the racemate resolve spontaneously into a racemic conglomerate, or will both enantiomers co-crystallize or co-adsorb forming racemic 3D or 2D crystals? In 3D (liquid) crystals, conglomerate formation is the exception[2, 3] rather than the rule. In 2D monolayers at the air/water interface, both the controlled separation of enantiomers and racemate formation have been reported from grazing incidence X-ray diffraction studies.[4, 5] In 2D monolayers on solid supports, modern tools such as atomic-force microscopy (AFM)[6] and scanning tunneling microscopy (STM) provide compelling evidence for spontaneous segregation.[7] The use of STM is especially appealing for the visualization of (sub)monolayer structures, since it can reveal with near-atomic resolution the ordering in two dimensions.[8] The technique has shown that both chiral[9–11] and achiral[12, 13] molecules self-assemble into chiral arrays, the former enantiospecifically and the latter as 2D conglomerates. Experimental data available so far suggest a spontaneous resolution,[9a, 10, 11a–d] although one report has noted differences in the way molecules discriminate through their chirality depending upon their absorption site.[14]

The compounds we have targeted to address these questions are the achiral formamide **1** and the chiral formamide **2**.[15] Here we report the X-ray crystal structure and STM imaging of the self-assembled monolayers of the enantiopure and racemic **2**, as well as the STM data for **1**, and compare the expression of molecular chirality in two and three dimensions.



R = H; **1**
R = Me; **2**

The X-ray crystal structure[16, 17] of the enantiopure compound (*R*)-**2** (Figure 1) has a unit cell which contains molecules with four different conformations, all of which form chains (in which the molecules are linked through N–H$\cdots$O=C and other weaker hydrogen bonds) that unite head-to-head through C–H$\cdots$O=C hydrogen bonds between formyl groups to generate supramolecular tapes. There are

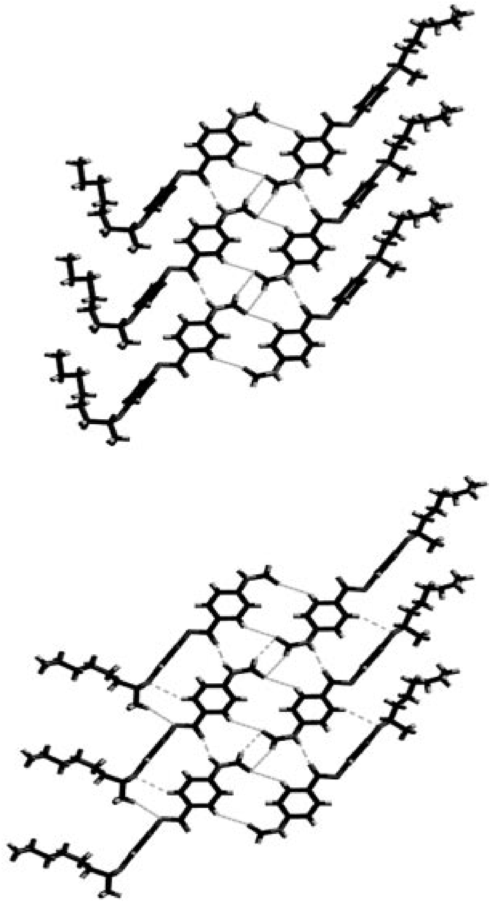


Figure 1. Views of the two hydrogen-bonded tapes formed by the four conformational diastereomers of (*R*)-**2** in its crystals. Intrachain N–H$\cdots$O distances: 2.072 and 1.940 Å; angles: 167.4 and 157.9°; N$\cdots$O distances: 2.864 and 2.857 Å; interchain C=O$\cdots$H–C distances: 2.685, 2.693, 2.675, and 2.686 Å; C–H$\cdots$O angles: 147.5, 147.4, 146.8, and 145.3°; C$\cdots$O distances: 3.514, 3.521, 3.500, and 3.500 Å.

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[*] Prof. Dr. F. C. De Schryver, Dr. S. De Feyter, A. Gesquière
Laboratory of Molecular Dynamics and Spectroscopy
Department of Chemistry, Katholieke Universiteit Leuven
Celestijnenlaan 220F, 3001 Heverlee (Belgium)
Fax: (+32) 16-327989
E-mail: frans.deschryver@chem.kuleuven.ac.be

Prof. J. Veciana, Dr. D. B. Amabilino
Organic Materials Laboratory
Institut de Ciència de Materials de Barcelona (CSIC)
Campus Universitari, 08193 Bellaterra (Spain)
Fax: (+34) 93-5805729
E-mail: vecianaj@icmab.es

Dr. K. Wurst
Institut für Allgemeine Anorganische und Theoretische Chemie
Universität Innsbruck
6020 Innsbruck, Innrain 52a (Austria)

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two types of gross conformations among the four molecules: one in which the aliphatic chain extends in the plane of the phenyl group to which it is attached, and one in which it is oriented approximately perpendicularly to this plane. None of the alkyl chains have the all-*trans* conformation, but instead contain portions with cisoid geometry. The reason for this distortion may result from the packing of the tapes, which allows only minimal interdigitation of the aliphatic chains.

The X-ray crystal structure[17, 18] of racemic **2** has a unit cell comprised of two centrosymmetrically related molecules. These molecules form homochiral chains (Figure 2) connected through various hydrogen bonds to give a very similar chain assembly as that of the enantiopure compound. These homochiral chains form heterochiral tapes. The alkyl chains (which are in the all-*trans* conformation) of neighboring chains interdigitate, with a minimum spacing between carbon atoms of adjacent chains of approximately 3.7 Å, to form sheets of molecules (Figure 2, top). There is strict *R*-*S*-*R*-*S* alternance within the sheets, which are not completely flat but undulate (Figure 2, bottom). Thus, there is no spontaneous resolution into enantiopure crystals in three dimensions but instead, racemic crystals are formed.

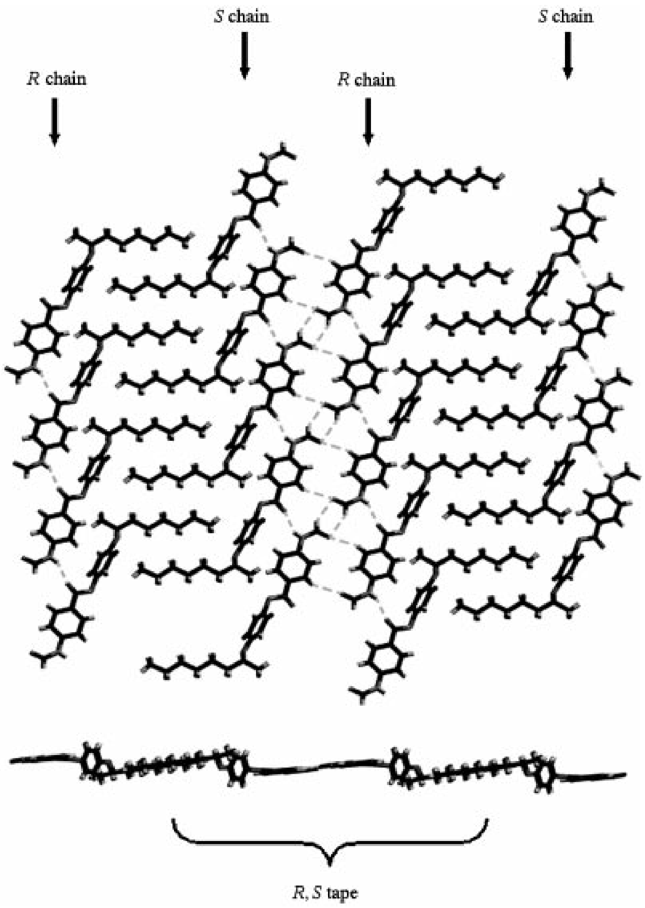

Figure 2. Views (top) perpendicular to a sheet of *rac*-**2** in its crystals showing the homochiral chains and heterochiral tapes and (bottom) parallel to the sheets showing their stepped nature with respect to the alkyl chain long axes. Intrachain N−H ⋯ O distance: 2.174 Å, angle: 149.8°, N ⋯ O distance: 2.888 Å, interchain C=O ⋯ H−C distance: 2.493 Å, C−H ⋯ O angle: 148.2°, C ⋯ O distance: 3.329 Å.

The self-assembly of the formamides **1** and **2** (in *S*, *R*, and *rac* forms) in two dimensions has been studied with STM at the 1-heptanol/graphite interface. All form monolayers with domains (areas of parallel tapes) which are related by the C_3 symmetry of the surface, and are characterized by areas of low tunneling current (observed as darker bands in the images) which correspond to the location of the alkyl chains (which are interdigitated) and brighter zones which coincide with the location of the phenyl benzoate moieties. Only in a few cases are the alkyl chains visible, which indicates there is a relatively high mobility. All the formamides self-assemble into tapes reminiscent of those in the crystal structures, with a distance between the same point in adjacent molecules within each chain of 8.60 ± 0.20 Å. The corresponding distance in the tapes of (*R*)-**2** and *rac*-**2** in their crystals are 8.66 and 8.86 Å, respectively. The repeat distance perpendicular to the tape direction is 29.0 ± 1.0 Å in the physisorbed monolayers, compared with 27.70 Å in the sheets formed in crystals of *rac*-**2**.

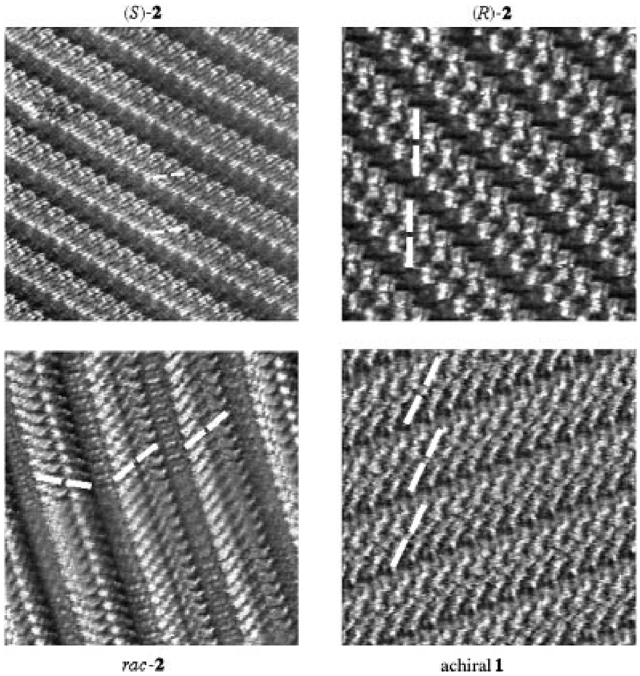

Figure 3. STM images of (*S*)-**2** (16.1 × 16.1 nm^2, 1.0 nA, −0.51 V; top left), (*R*)-**2** (12.0 × 12.0 nm^2, 1.0 nA, −0.73 V; top right), *rac*-**2** (13.6 × 13.6 nm^2, 1.0 nA, −0.54 V; bottom left), and **1** (11.3 × 11.3 nm^2, 1.0 nA, −0.83 V; bottom right) at the 1-heptanol/graphite interface. The orientation of some of the phenyl benzoate groups is indicated by a bar.

The images of monolayers of enantiopure formamides (*S*)-**2** and (*R*)-**2** (Figure 3) are enantiomorphous, while *rac*-**2** shows a very distinct structure. The chiral induction phenomenon for (*S*)-**2** and (*R*)-**2** in pure form is expressed by the orientation of the phenyl benzoate moiety with respect to the normal on the propagation direction of the tapes (the tape normal): the phenyl benzoate moieties are rotated clockwise for (*S*)-**2** and counter-clockwise for (*R*)-**2**. In order to judge the influence of the graphite substrate, the registration of the observed monolayers with respect to the surface has been determined and is expressed by the angle θ, that is, the angle between the propagation direction of the tapes and the reference axis along the [0010] direction of the graphite surface (Figure 4), which is almost parallel to the propagation direction of the tape. The angle θ takes negative and positive values for (*S*)-**2** and (*R*)-**2**, respectively (between 0° and 12° with a bias for larger values). Thus the molecular chirality of enantiopure **2** is expressed by both the orientation of the adlayer with respect to the symmetry of the underlying graphite lattice and by the orientation of the phenyl benzoate moieties with respect to the tape normal.

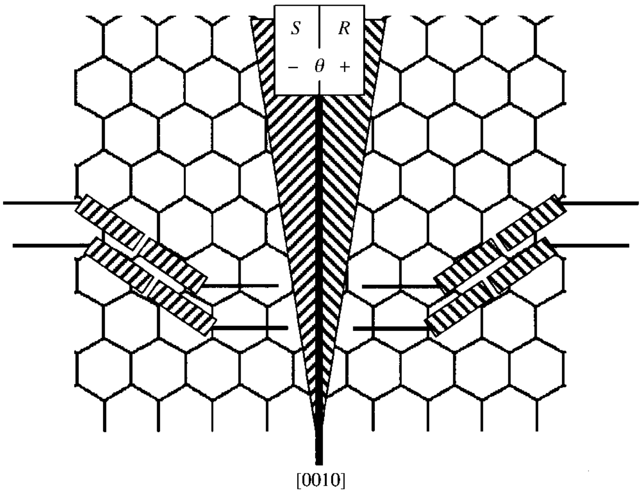

Figure 4. A schematic representation of the orientations of the molecules of (*S*)- (left) and (*R*)-**2** (right) at the graphite/1-heptanol interface.

The racemic mixture *rac*-**2** physisorbed from 1-heptanol on graphite (Figure 3) does not display the generally observed spontaneous resolution on surfaces. The angle θ is always found to be $0 \pm 1°$, which suggests there is a different packing of the tapes to those formed by the pure enantiomers. In addition, the phenyl benzoate groups within a domain are rotated both clockwise and anticlockwise from the tape normal, as can be appreciated clearly in the image shown in Figure 3. In a few cases it was possible to correlate details in the STM images with intermolecular features in great detail. For example, in a high-resolution image, such as Figure 5, the STM contrast in the upper area suggests that one of the phenyl rings of the phenyl benzoate groups is lying flat on the graphite surface while the other one is tilted. In general, the specific STM contrast on a (sub)molecular scale does not allow the chiral nature of a domain to be characterized. However, the two observations mentioned above, that is, the registry of the molecules with respect to the graphite surface and the orientation of the molecules with respect to the tape normal, do show that the domains formed by the racemate have the characteristics of neither the *R* nor *S* enantiopure domains, but are racemic themselves: domains formed from a racemate solution are not enantiomerically pure. To the best of our knowledge this is the first time that this finding has been reported for 2D adlayers adsorbed on a solid surface and studied by STM.

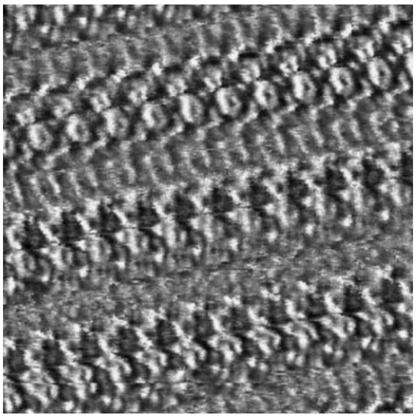

Figure 5. A high-resolution STM image of *rac*-**2** (9.6×9.6 nm^2, 1.0 nA, −0.58 V) at the 1-heptanol/graphite interface.

Two possibilities have to be kept in mind when considering the composition of the individual tapes in a racemic domain, firstly the tapes are enantiopure. In this case, although there is no segregation at the level of domains, there would be segregation at the tape level. From the orientation of the aromatic groups in Figure 3 (bottom left) the sequence of the chirality of the tapes can then be described as being (from left to right) *S*-*S*-*R*-*R*-*R*-*R* when our findings for the enantiopure compounds are taken into account. Secondly the tapes are racemic, as in the 3D crystals. To achieve this packing the *R* and *S* enantiomers have to lie head-to-head, and the long axes of the aromatic groups have to be oriented along the same line. The resulting arrangement is similar to the one shown in Figure 2. This centrosymmetrical arrangement requires that one enantiomer has a methyl group (attached to the stereogenic center) pointing towards the graphite surface, which is energetically unfavorable.[19]

A final result which is important to highlight is that, in stark contrast to racemic **2**, the achiral compound **1**[20] exhibits enantiomorphic domains that always consist of only one of the two possible orientations of the aromatic groups with respect to the tape axis (Figure 3, bottom right) and the angle θ takes positive or negative values (never 0°), that is, this achiral compound shows segregation and the formation of chiral domains.

The type of structural resemblance between X-ray structures and physisorbed monolayers, as seen here for *rac*-**2**, is rare,[21–23] but provides important clues regarding the roles of each structural feature of the molecule in self-assembly processes. The conformational mobility of the chiral alkyl chains in this interesting family of compounds allows the formation of different unions between the hydrogen-bonded tapes in the crystals and on the graphite substrate; the subtle interactions of the latter with the tapes must surely play an important role. The tapes described here are clearly robust "supramolecular synthons",[24] both on the graphite surface and in the crystals. It has been shown that a racemic mixture does not show segregation in two dimensions but forms a racemate. This observation might have important implications concerning the expression of stereochemistry at surfaces and its transfer into three dimensions.

Experimental Section

Compounds **1** and **2** were prepared according to the published method.[15] The STM images were acquired in the variable current mode (constant height) under ambient conditions with the tip immersed in the liquid. For details see ref. [9].

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[16] X-ray structural data for (*R*)-**2** at 223 K: colorless plate, radiation used $Mo_{K\alpha}$, empirical formula $C_{22}H_{27}NO_4$, triclinic, space group $P\bar{1}$ (No. 1), $a = 8.6598(3)$, $b = 8.6770(4)$, $c = 29.688(2)$ Å, $\alpha = 95.411(2)$, $\beta = 94.923(3)$, $\gamma = 110.092(3)^\circ$, $V = 2069.0(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.186$ g cm^{-3}. $F(000)$ 792, $\theta = 2.52 - 21.99^\circ$, unique reflections measured 7326, unique reflections observed $(I > 2\sigma) = 5758$, parameters 989, restraints 3, *R* indices (all data) 0.0795, *wR*2 (all data) 0.1442, final *R* indices $(I > 2\sigma(I)) = 0.0564$, final *wR*2 $(I > 2\sigma(I)) = 0.1283$.

[17] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-159907 and CCDC-159908. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[18] X-ray structural data for *rac*-**2** at 223 K: colorless prism, radiation used $Mo_{K\alpha}$, empirical formula $C_{22}H_{27}NO_4$, triclinic, space group $P\bar{1}$ (No. 2), $a = 8.856(1)$, $b = 9.543(2)$, $c = 12.604(2)$ Å, $\alpha = 94.885(6)$, $\beta = 106.972(9)$, $\gamma = 98.526(9)^\circ$, $V = 998.2(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.229$ g cm^{-3}, $F(000)$ 396, $\theta = 1.71 - 19.87^\circ$, unique reflections measured 1762, unique reflections observed $(I > 2\sigma) = 1226$, parameters 249, restraints 0, *R* indices (all data) 0.0857, *wR*2 (all data) 0.1580, final *R* indices $(I > 2\sigma(I)) = 0.0534$, final *wR*2 $(I > 2\sigma(I)) = 0.1343$.

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