Monolayers of Macrocyclic Polyamides at the Air–Water Interface

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The poly-*N*-acylated derivatives (**1b**), (**1c**), (**1d**), and (**2d**) of the macrocyclic polyamines [18]-N_6 (**1a**) and [30]-N_{10} (**2a**) form Langmuir monolayers in which the macrocycle lies flat on the water surface while the alkane chains tilt upright in the compressed film.

Macrocyclic polyamines bearing long chains on the nitrogen sites yield mesomorphic phases in which the rings are stacked, thus forming a tube-like molecular array (tubular mesophases).[1] The presence in such molecules of hydrophilic (amide linkages) and hydrophobic (alkane chains) groups led us to expect that they should spread as Langmuir monolayers.[2] We report here that this new class of amphiphiles indeed form monomolecular films at the air–water interface.†

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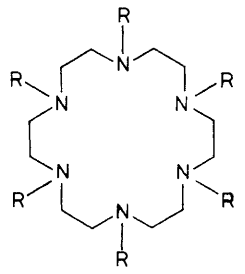
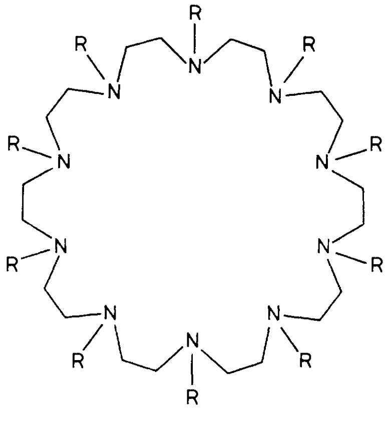
† Monolayers incorporating different types of cyclic compounds have been described: porphyrins,[3] phthalocyanines,[4] disc-shaped molecules,[5,6] cyclodextrins,[7] and calixarenes.[8]



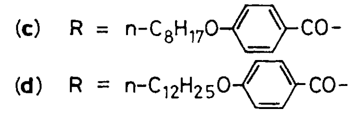
(1)



(2)

(a) R = H

(b) R = n-$C_{11}H_{23}CO$-



(c) R = n-$C_8H_{17}O$-C_6H_4-CO-

(d) R = n-$C_{12}H_{25}O$-C_6H_4-CO-

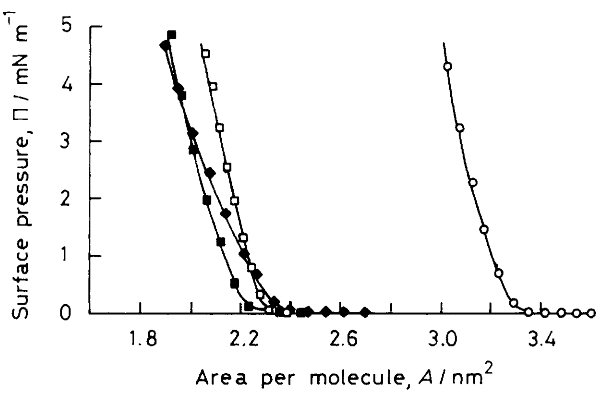


Figure 1. Surface pressure–area diagrams for (**1b**) (◆), (**1c**) (□), (**1d**) (■) and (**2d**) (○), at 14.5 °C.

Table 1. Transition temperatures and enthalpies for compounds (**1b**), (**1c**), (**1d**) and (**2d**).[a]

Compound	
(**1b**)	$K \xrightarrow[33.4]{106.5} I$
(**1c**)	$K \xrightarrow{120} T \xrightarrow[0.9]{139} I$
(**1d**)	$K \xrightarrow[35.7]{121.5} T \xrightarrow[0.7]{141.5} I$
(**2d**)	$K \xrightarrow[36.3]{187} I \xrightarrow[(2.5)]{(145.5)} T$

[a] Temperatures are in °C and enthalpies (italics) in kcal mol⁻¹ (1 kcal = 4.184 kJ); K: crystal; T: tubular mesophase; I: isotropic liquid; ( ): monotropic transition temperature.

Table 2. Areas per molecule (*A*) and molecular diameters (*D*) derived from experiments at the onset of the transition between the expanded and the condensed states of the monolayer.

Compounds	A/Å², ±5	D/Å, ±0.2
(**1b**)	235	17.3
(**1c**)	230	17.1
(**1d**)	225	16.9
(**2d**)	335	20.6

The four poly-*N*-acylated derivatives investigated, (**1b**), (**1c**), (**1d**), and (**2d**), were prepared as already described[1] by reaction of the macrocyclic polyamines [18]-N_6 (**1a**) (Fluka AG) or [30]-N_{10} (**2a**)[9] with 6 or 10 equiv. of acid chloride (n-$C_{11}H_{23}COCl$, *p*-n-$C_8H_{17}O$-C_6H_4-COCl, or *p*-n-$C_{12}H_{25}O$-C_6H_4-COCl) in dry dimethylacetamide in the presence of 6 or 10 equiv. of *p*-dimethylaminopyridine. Water was added and the precipitate was separated. The crude macrocyclic polyamides were purified by t.l.c. (silica gel, eluent: chloroform + 5—10% methanol depending on the polyamide; about 80% yield) and recrystallized from methanol–diethyl ether (60—70% overall yield).‡ The transition temperatures and enthalpies for these materials are given in Table 1.

Compound (**1b**) is devoid of mesomorphism whereas the three benzoyl derivatives (**1c**), (**1d**), and (**2d**) exhibit a tubular phase. The appearance of this mesophase must be connected with the presence of a dense aromatic crown made rigid by the amide linkages. Only the benzoyl derivatives of the smallest macrocycle, [18]-N_6 (**1c**) and [18]-N_6 (**1d**), display a stable tubular mesophase. Moreover, as previously noted for (**1d**),[1] the lattice constant of (**1c**) (32.7 Å),[10] *i.e.* the distance between the cores of two adjacent columns of the hexagonal tubular phase is smaller than the diameter (40 Å) of the hexamide measured on a molecular model.

Monolayers were formed in the usual way by spreading the macrocyclic polyamides from dichloromethane solutions (about 0.2 mg ml⁻¹) at the air–water interface of a Langmuir trough. Surface pressures were measured by the Wilhemy hanging plate. The set-up employed can measure surface pressure down to 10 μN m⁻¹ with a sensitivity of 1 μN m⁻¹. Surface concentration was continuously varied using a computer-controlled, movable Teflon barrier, taking care to maintain thermodynamic equilibrium.[11] Surface pressure *vs.* surface concentration measurements were repeated at least three times for each sample. The reproducibility of the data was about 5%. The film balance used was specially fitted for measuring very weak surface tensions. Consequently, we first examined the pressure below 5 mN m⁻¹, *i.e.* before reaching the collapse point.§

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‡ Satisfactory elemental analysis results were obtained for (**1b–d**) and (**2d**). (**1b**): ¹H n.m.r. [($CDCl_3$), 200 MHz, 22 °C]; δ 0.88 (18H, t, CH_3), 1.25 (96H, m, CH_2), 1.61 (12H, m, CH_2CH_2CO), 2.38 (12H, m, CH_2CO), 3.45 (24H, m, CH_2N). (**1c**): ¹H n.m.r. [($CDCl_3$), 200 MHz 22 °C]; δ 0.89 (18H, t, CH_3), 1.30 (60H, m, CH_2), 1.79 (12H, m, CH_2CH_2O), 3.71 (24H, m, CH_2-N), 3.95 (12H, t, CH_2O), 6.84 (12H, d, ArH), 7.26 (12H, d, ArH). (**1d**): ¹H n.m.r. [($CDCl_3$), 200 MHz, 22 °C]; δ 0.88 (18H, t, CH_3), 1.27 (108H, m, CH_2), 1.78 (12H, m, CH_2-CH_2O), 3.73 (24H, m, CH_2-N), 3.95 (12H, t, CH_2O), 6.84 (12H, d, ArH), 7.26 (12H, d, ArH). (**2d**): ¹H n.m.r. [(hexachlorobutadiene), 200 MHz, 110 °C]; δ 0.88 (30H, t, CH_3), 1.28 (180H, m, CH_2), 1.71 (20H, m, CH_2CH_2O), 3.55 (40H, m, CH_2N), 3.86 (20H, t, CH_2O), 6.72 (20H, d, ArH), 7.22 (20H, d, ArH).

§ A break in the Π–*A* diagram was observed in the case of compound (**1b**) for upper pressures (see also ref. 12), but this feature requires further careful investigation because of the long time of mechanical equilibration (about one hour per single run).

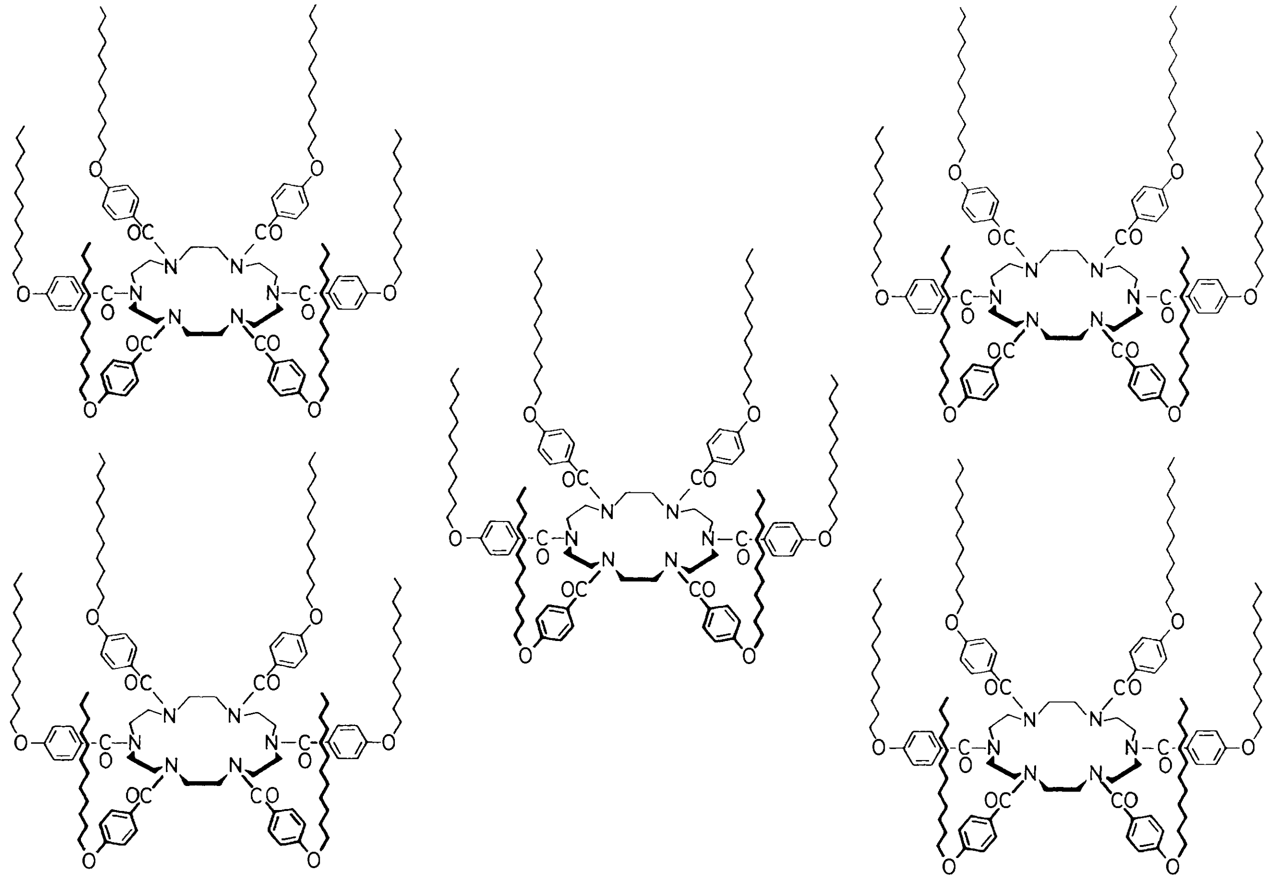

Figure 2. Schematic representation of the arrangement of macrocycle (**1d**) in a compressed film at the air–water interface. The aliphatic chains have been represented in their extended form, but of course some degree of curling up may occur.

Surface pressure (Π) *vs.* area per molecule (*A*) diagrams of (**1b**), (**1c**), (**1d**), and (**2d**) (Figure 1) indicate that defined monolayers are formed at 14.5 °C. Areas per molecule and molecular diameters *D* derived from experiments are given in Table 2 where $D = (4A/\pi)^{\frac{1}{2}}$ for polar fragments having a circular shape. The apparent diameters of (**1c**) and (**1d**) are almost identical (~17 Å) and correspond to that determined on molecular models for the hexabenzoyl derivative of macrocycle [18]-N_6 (**1a**) with an open central cavity (Table 3). The macrocycles thus lie flat on the water surface owing to the polar water-attracting amide groups and the aliphatic chains tilt towards a vertical orientation, relative to the air–water interface, upon compression (Figure 2). The same holds for the larger macrocycle (**2d**); the ten alkoxy chains stand up from the decabenzoyl macrocyclic core (~21 Å diameter), which lies flat on the water surface.

On the other hand, the apparent diameter *D* of (**1b**) (~17 Å) corresponds to the six lauroyl chains being bent into the upright position from the third methylene group (see Table 3). The smaller upward slope of the Π–*A* diagram of (**1b**) compared to the other polyamides (Figure 1) is probably due to the absence of the crown of benzoyl groups which makes the macrocycle rigid. At lower temperature (2.1 °C), the Π–*A* diagram of (**1b**) shows an increase in surface pressure with lower surface concentration, compared to 14.5 °C; this may result from a freezing of conformational mobility in the aliphatic chains.

The monolayers formed by molecules (**1b**—**d**) and (**2d**) present an array of macrocyclic units at the air–water interface (for a recent study of similar systems see ref. 12). Since macrocyclic molecules may form complexes with a number of substrates, in particular with metal ions, it is of interest to study the effect of such species present in the water phase on the properties of the molecular film. In view of the binding selectivities shown by macrocyclic ligands, the monolayers which they form may present substrate dependent properties, thus endowing these molecular assemblies with molecular recognition features at an interface (of interest, for instance, for selective detection).

Table 3. Molecular diameters (Å) for various lengths of R, measured on Corey–Pauling–Koltun atomic models (the values in bold type correspond to the diameters of Table 2).[a]

	Structure	
R	(1)	(2)
H (central cavity)	2	5.5
-CO-	13.5	15.0
$-CO-CH_2-CH_2-$	**17.0**	—
$-CO-p-C_6H_4-$	**16.9**	**20.8**
$-CO-(CH_2)_{10}-CH_3$	40.0	—
$-CO-p-C_6H_4-O-n-C_8H_{17}$	40.0	—
$-CO-p-C_6H_4-O-n-C_{12}H_{25}$	50.5	55.5

[a] Aliphatic chains taken in their extended state.

We thank Dr. M. W. Hosseini for a sample of compound (**2a**).[9]

Received, 20th February 1989; Com. 9/00765B

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