Chiral Discrimination of Monosaccharides by Monolayers of a Steroidal Boronic Acid

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The relationship between molecular structure and physical properties of monolayers of complexes between an amphiphilic, steroidal cholesterol-substituted phenylboronic acid (**1**) and monosaccharides was studied at the air–water interface. Phase transition, compressibility and limiting molecular area of monolayers of **1** in the presence of monosaccharides are correlated with the calculated structures of the phenylboronic acid–monosaccharide complexes. The monolayer of **1** exhibits chiral discrimination towards optical isomers of monosaccharides. The phase transition during compression of monolayers of **1** is discussed to reflect rearranged binding positions between the boronic acid and monosaccharides.

The chiral recognition of molecules with biological relevance such as sugars, amino acids *etc.* is of great importance. Recently, the artificial receptor **1** (Fig. 1) consisting of a phenylboronic acid linked to a cholesterol moiety was shown by a spectroscopic method to meet this requirement.[1] When inserted into a cholesteric liquid crystal, the complexes are divided into two groups, one stabilizing the cholesteric liquid crystal and the other destabilizing the cholesteric liquid crystal (as indicated by a blue shift and a red shift, respectively, of the reflectance maxima). The interaction between phenylboronic acids and diols[2–4] as well as sugars and related compounds has been studied over the past few years.[5–17] These studies established not only the structure of the complexes but quantified their stability[5–7] and showed possible applications for membrane transport,[8,9] sensors,[10] matrix-supported receptors[11,12] or boron neutron capture therapy[17,18] as well. A number of phenylboronic acids[1,14,15] and diphenyldiboronic acids[5,16] possess unique properties such as high sensitivity towards sugars together with pronounced selectivities for mono- and disaccharides due to facile complexation between boronic acids and 1,2- or 1,3-diols not only in organic and aqueous alkaline, but also in neutral solutions.[15] In contrast to these boronic acids, compound **1** unites two outstanding characters which prompted us to attempt chiral recognition of sugars at the air–water interface, *i.e.* (i) it can form stable monolayers[19,20a,21] and (ii) the steroidal lipophilic moiety is chiral. The air–water interface is a suitable medium for chiral recognition, as shown in the case of monolayers of enantiomeric stearoylserine and amino acid esters,[22,23] phospholipid monolayers[24] as well as polymeric Langmuir–Blodgett (LB)-films containing chiral groups.[25] We report here about the unique correlation between monolayer properties of **1** in the presence of monosaccharides in the subphase and the structure of complexes of **1** with these sugars.

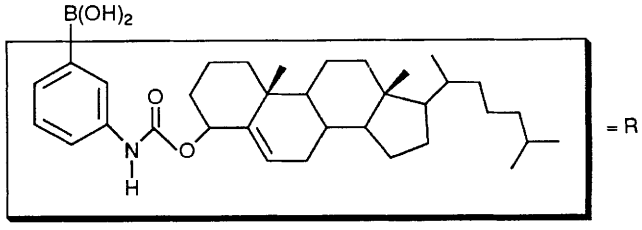

Fig. 1 Structure of compound **1**

Experimental

The synthesis of **1**, the structure of the complexes in non-aqueous media including their Ph–Ph angle and their spectroscopic properties were published earlier.[1] For the present study, monolayers of **1** were prepared by spreading a benzene–chloroform (4:1 v/v) solution on a subphase containing K_2CO_3 (18 mmol dm^{-3}) and monosaccharide (11 mmol dm^{-3}; pH = 10.4) unless otherwise stated. At this pH, the boron atom in **1** is sp^3-hybridized. Pressure–area (π–A) isotherms were measured at 293 and 303 K and a barrier speed of 36 cm^2 min^{-1} (0.4 mm s^{-1}) with an computer-controlled FSD-20 type film balance (USI Corp.) on an air-suspended table in a clear-air zone according to the Wilhelmy-method. The experimental conditions for measuring π–A isotherms including compression speed and temperature were carefully maintained constant for all measurement series in order to obtain reproducible isotherms. Saccharides (Fluka, for microbiology, ratio of anomers not specified) were used without further purification. Water was filtered, ion exchanged and bidistilled (Barnstead). The trough size and the maximum area before compression were 0.071 m^2 and 0.95 nm^2 molecule $^{-1}$, respectively. The spreading solvents were allowed to evaporate within 15 min. All solutions were freshly prepared. Isomerization and epimerization[26] (mutorotation) reactions involving the monosaccharides in the subphase were not observed under the experimental conditions [low concentrations of boronic acid (10^{-4} mmol) and saccharides (5.5 mmol), measurement time 30 min and pH below 11] within 1 h, but affected the π–A isotherms 1 day after sample preparation. The stability was confirmed in previous studies at low concentrations.[14–16] Negative secondary ion mass spectra ($SIMS^-$) were recorded on a M-2500 mass spectrometer (Hitachi).

Semiempirical molecular orbital calculations (AM1 method[27]) of the simplified complexes between monosaccharides and non-substituted phenylboronic acid were performed in order to evaluate the energy and structure of these complexes. At first, all possible conformers of monosaccharides and sp^2- or sp^3-hydridized phenylboronic acid units were established independently by using the molecular modelling system MOLGRAPH.[28] As the second step, the input structures for calculations were obtained by using the same system and combinations of these moieties considering the binding positions and the conformation of the complexes. These structures were fully optimized with MOPAC[29] version 6.0 using the AM1 Hamiltonian. The Ph–Ph dihedral angles

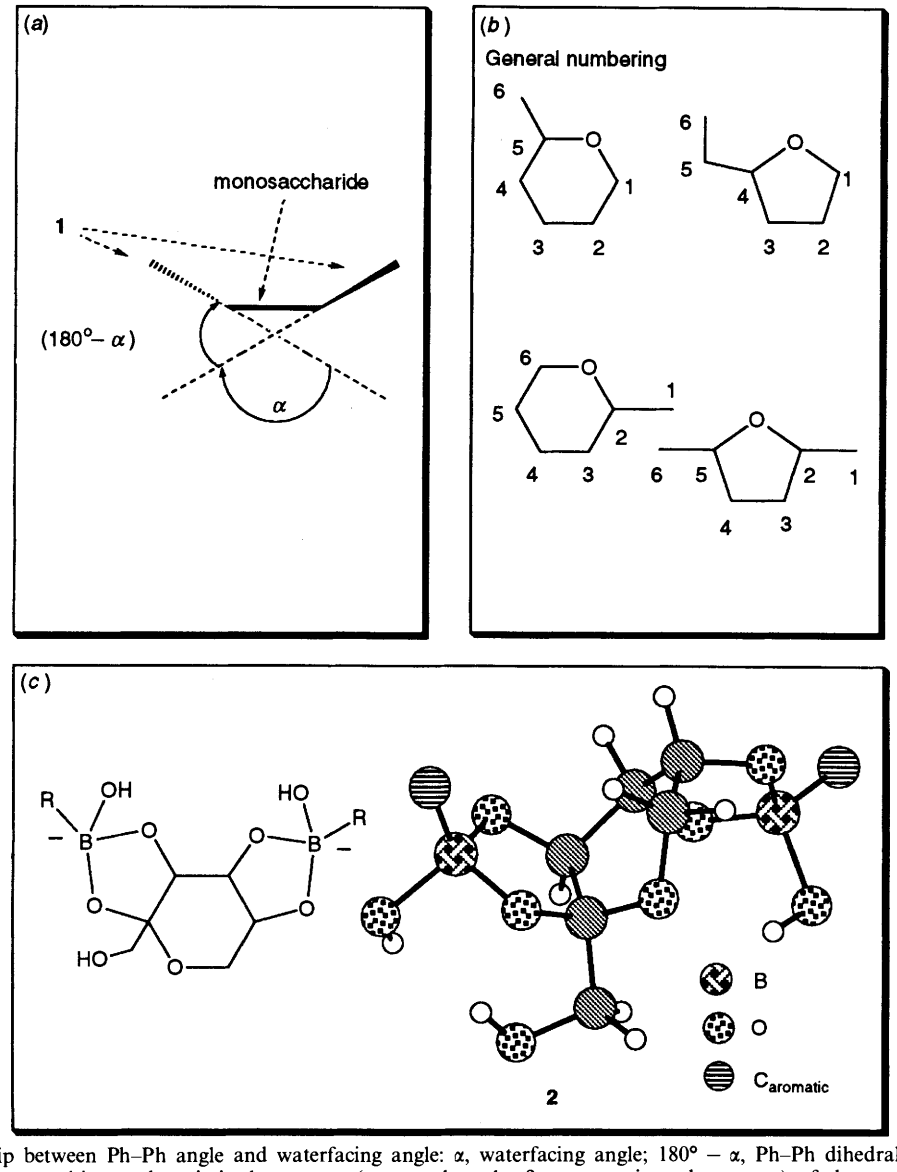

Fig. 2 (*a*) Relationship between Ph–Ph angle and waterfacing angle: α, waterfacing angle; 180° – α, Ph–Ph dihedral angle. (*b*) Numbering scheme. (*c*) Proposed composition and optimized structure (truncated at the first aromatic carbon atom) of the complex **2** between **1** and D-fructopyranose at the air–water interface.

formed between two mean planes of phenyl units were calculated for the optimized structures. Calculations were carried out on an engineering workstation SUN 4/2 and IRIS 4D 35G.

Results and Discussion

Structure of the Complexes between **1** *and Monosaccharides.*— From the ^{1}H NMR spectra [14] of extracted complexes involving phenylboronic acid **1** and D-fructose or D-glucose as well as from semiempirical molecular orbital calculations (AM1) [1] a stoichiometry of 1:2 (monosaccharide:phenylboronic acid) of the complexes with the monosaccharides in the pyranose form was concluded. The calculation also revealed the Ph–Ph dihedral angle of several complexes which ranges from 0 to 90°. For the present study, the complement to 180° of the Ph–Ph angle is employed in the discussion, because this 'waterfacing' angle of the phenyl rings illustrates the structure at the air–water interface clearly. Fig. 2 depicts the fructopyranose complex as an example and the relationship between Ph–Ph angle and waterfacing angle.

Different from the non-aqueous system, monosaccharides preferably exist as furanoses in boric acid complexes in aqueous alkaline bulk solution, where the boron atom is sp^3-hybridized.[30] In contrast to that, the pyranose form exists in monosaccharide complexes of **1** in non-aqueous media. For the present study, two series of calculations are taken into account for model compounds of all experimentally studied monosaccharide complexes of **1** in order to determine their waterfacing angle: (i) sp^2-hybridized boron and pyranoses, because these complexes are most stable in non-aqueous solvents and the air–water interface provides an environment different from aqueous bulk solution and (ii) sp^3-hybridized boron atom and furanoses, because these complexes are more stable in aqueous alkaline solution, and the pH of the subphase was higher than pK_a (pK_a *ca.* 9). In order to decide if the complexed monosaccharide is pyranose or furanose at the air–water interface, the experimental results described below are compared with the two different structural approaches. Selected optimized structures and their heat of formation *E* are included in Table 1.

In order to prove the stoichiometry at the air–water interface to be the same as in homogeneous solution and in the case of two-phase solvent extraction, where the monosaccharide bridges two phenylboronic acid molecules,[1] the monolayer of **1** on a 22 mmol dm^{-3} fructose containing subphase was transferred by the Langmuir–Blodgett (LB) method during 80 cycles by vertical dipping at 293 K and 35 mN m^{-1} onto a surface-modified steel plate (60 mm^2) suitable for mass spectroscopy. The initial transfer ratio was 1.0. The $SIMS^-$

spectrum is depicted in Fig. 3 in part, where an asterisk marks FOMBLIN® peaks arising from the calibration prior to the measurements. The following species involving the complex **2** were detected and marked with an arrow in Fig. 3: $[\mathbf{2} + K + H_2O]^-$, $[\mathbf{2} + K + 2H_2O]^-$, $[\mathbf{2}]^{2-}$ and $[\mathbf{2} + 2H_2O]^{2-}$ with m/z = 1273, 1291, 608 and 626, respectively. The structure of **2** is indicated in Fig. 2 for fructopyranose. No evidence for the formation of a 1:1-complex was found in the mass spectrum. The charge of the species indicate sp^3-hybridization of the boron atom. The results support the view that **1** forms 1:2 (monosaccharide:**1**) complexes not only in solution but at the air–water interface as well. We consider this to be important for discussing the correlation between molecular structure and certain monolayer properties.

Table 1 Selected complexes and their calculated heat of formation E

Saccharide	Boron	Binding site	E/kJ mol^{-1}
Fructopyranose	sp^2	1,2–4,5	−1227.50
Fructopyranose	sp^2	2,3–4,5	−1227.38
Fructopyranose	sp^2	1,3–4,5	−1198.17
Fructofuranose	sp^2	1,2–4,5	−1175.63
Fructofuranose	sp^2	2,3–4,6	−1161.55
Fructofuranose	sp^2	1,3–4,6	−1115.25
Glucopyranose	sp^2	1,2–4,6	−1223.61
Glucopyranose	sp^2	1,2–3,6	−1189.12
Glucopyranose	sp^2	1,2–3,4	−1168.00
Glucofuranose	sp^2	1,2–5,6	−1236.97
Glucofuranose	sp^2	1,2–3,5	−1225.99
Fructofuranose	sp^3	1,2–4,6	−1970.22[a]
Fructofuranose	sp^3	2,3–4,6	−1951.87[b]
Glucofuranose	sp^3	1,2–5,6	−2032.78[c]

[a,b,c] Maximum difference in energy for the four conformers at the sp^3-boron atoms is: (*a*) 0.8 kJ mol^{-1}, (*b*) 1.7 kJ mol^{-1} and (*c*) 8.0 kJ mol^{-1}.

Monolayer Properties.—Fig. 4 shows typical examples of π–A isotherms of **1** in the presence of monosaccharides. The molecular area of these isotherms was calculated on the basis of the monomeric phenylboronic acid. Since the monolayer consists of complexes in which two phenylboronic acid molecules are bridged, the molecular area of the complex is twice that value. A transition in compressibility at around 0.39 ± 0.01 nm^2 molecule^{-1} is interpreted as a transition from an expanded phase to a condensed phase according to the shape

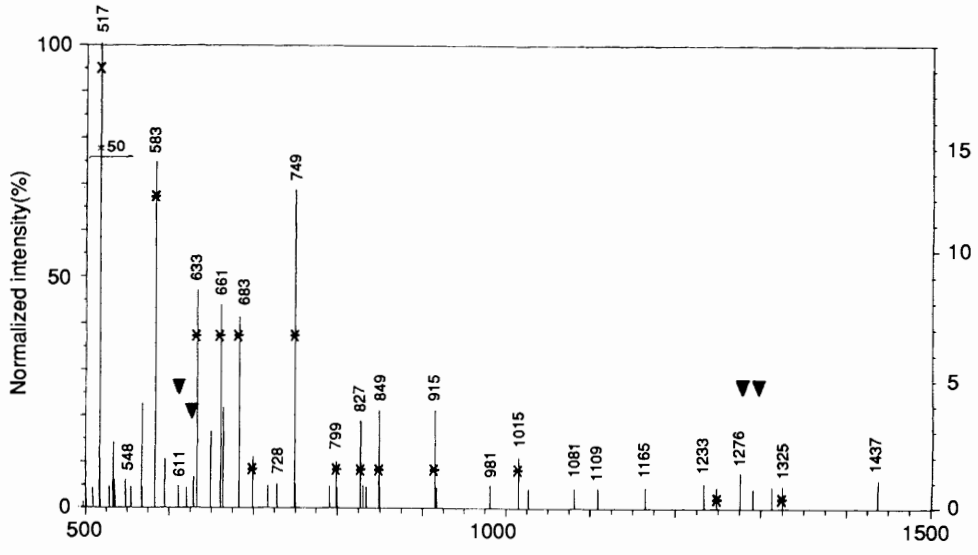

Fig. 3 SIMS$^-$-spectrum of the fructose–**1** complex at the air–water interface after transfer to a steel plate by using the LB-method

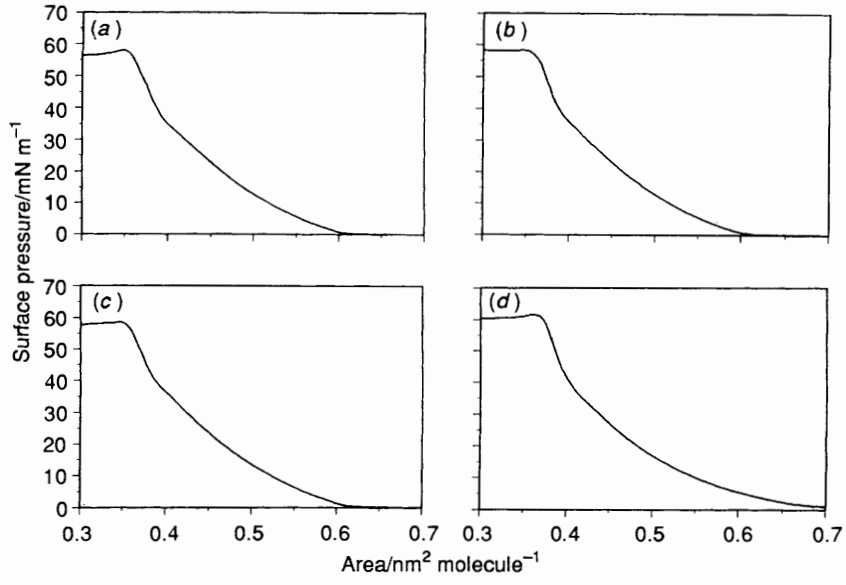

Fig. 4 Typical pressure–area isotherms of **1** at 303 K and pH 10.4 in the presence of 11 mmol dm^{-3} monosaccharide in the subphase: (*a*) D-glucose; (*b*) D-mannose; (*c*) D-galactose: (*d*) D-xylose

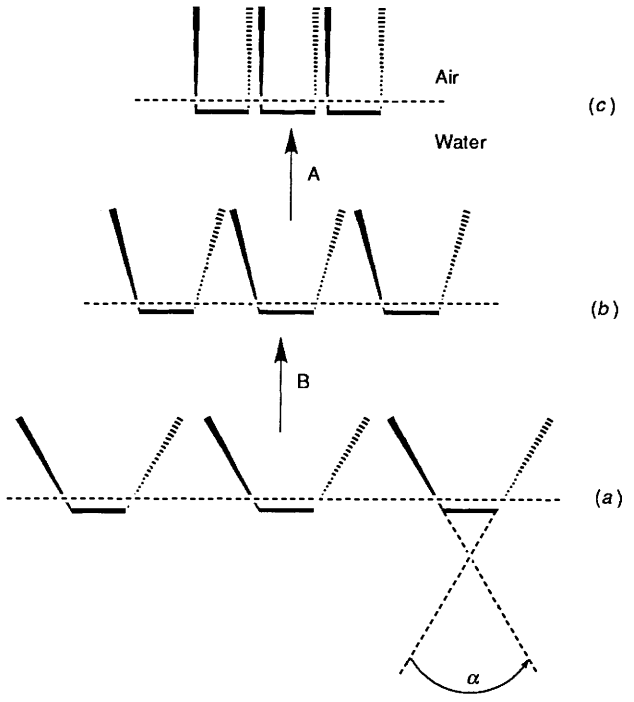

Fig. 5 α = Water-facing angle. (*a*) Expanded monolayer, surface pressure zero; (*b*) partly compressed monolayer, **1** is still flexible; (*c*) rigid monolayer before collapse.

of the π–A isotherms. The surface pressure where this transition takes place (transition pressure) obviously depends on the structure of the monosaccharide. The increase in compressibility up to the transition can be ascribed to the increasing packing density in the monolayer due to the rotational and torsional freedom of **1**. From CPK-models the minimum area occupied by a cholesterol-substituted phenylboronic acid molecule was estimated to be about 0.45 nm^2. This value is in good agreement with the limiting area determined by extrapolation of the π–A isotherms after the transition, ranging from 0.44 to 0.50 nm^2 in the presence of 11 mmol dm^{-3} of monosaccharides. Above the transition pressure the cholesterol moieties are therefore assumed to achieve highest packing density and an orientation parallel to each other. Fig. 5 depicts the simplified change in packing density accompanied by structural changes during compression. Although the single bonds cause considerable rotational and torsional freedom in **1**, it is impossible to achieve the highest packing density without changing Ph–Ph dihedral angle and the structure of the complex. Some examples for the energy ΔE necessary for a structural change can be derived from the values of E in Table 1. On the other hand, the free energy ΔG during compression can be calculated by integration of a π–A isotherm with π ranging from zero to the transition pressure according to eqn. (1).[31] A value of 23 kJ mol^{-1} is obtained for

$$\Delta G_T = \int A \, d\pi \qquad (1)$$

the complex with D-mannose as an example. The order of magnitude of this energy is sufficient to rearrange the structure and the binding position. Thus, the packing density in the monolayer is also changed. Another effect observed during the preparation of LB-films of the fructose-complex at constant pressure supports the above-mentioned conclusions: even several mN m^{-1} below the transition pressure, the surface pressure decreased within a few minutes and reached a new constant value when the area was kept constant. The structure of the complexes changes with the surface pressure. This also explains why the transition in the isotherms is not

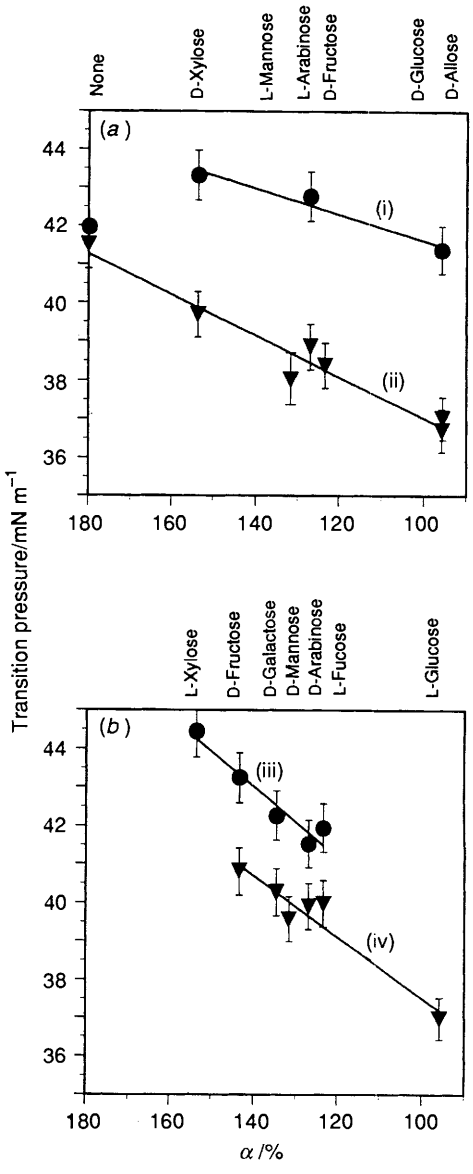

Fig. 6 Plots of surface pressure of monolayers of complexed **1** at phase transition *vs.* the waterfacing angle α of the complexes which destabilize (*a*) or stabilize the cholesteric liquid crystals (*b*). The points are the average of 2 to 3 experiments. ●, 293 K; ▼, 303 K. R = (i) 0.96, (ii) 0.9, (iii) 0.93, (iv) 0.9.

a sharp point, but takes place in a certain range of surface pressure.

In Fig. 6 the transition pressure of the investigated monolayers is plotted as a function of the waterfacing angle α between the two phenyl moieties in the complexes involving the pyranose form of monosaccharides. Table 2 summarizes the values of α for the optimized structures of the corresponding complexes. The angles were obtained by means of MO (AM1)-calculations. The angles in the pyranose series were previously shown to correlate with the shift in the reflectance maximum of cholesteric liquid-crystals induced by the presence of 1.2 or 2.4 mol% of **1** complexed with monosaccharides.*

* The waterfacing angle α between two cholesterol moieties calculated for the linear sp^2-hybridized boron is the same as the average of the two possible angles calculated for the planar sp^3-hybridized boron atom, though the heat of formation of the complexes is quite different. Therefore, it is possible to discuss the angle of the complexes with sp^2-hybridization of boron even for an aqueous alkaline environment, where the boron is negatively charged as concluded from the $SIMS^-$-spectra.

Table 2 Waterfacing angles of the complexes between **1** and monosaccharides in the pyranose or furanose form for the MO-optimized structures

Saccharide	Binding site	∠(p)[a]	Binding site	∠(f)[b]
Xylose	1,2–3,4	153.5	1,2–3,5	93.2
Fructose	2,3–4,5	143.3	1,2–4,6	115.3
Galactose	1,2–4,6	134.6	1,2–5,6	132.3
Mannose	2,3–4,6	131.6	2,3–5,6	166.7
Arabinose	1,2–3,4	126.9	1,2–3,5	103.5
Fucose	1,2–3,4	123.3	1,2–3,5	100.9
Glucose	1,2–4,6	95.8	1,2–5,6	145.5
Allose	2,3–4,6	95.6	2,3–5,6	119.1

[a] ∠(p), calculated angle of pyranose complexes. [b] ∠(f), calculated angle of furanose complexes.

It is seen from Fig. 6, that the complexes are clearly divided into two groups according to their structure. Those causing a red shift in the cholesteric liquid crystal system and destabilizing it (D-xylose, L-mannose, L-arabinose, D-fucose, D-glucose and D-allose) fit a linear plot in Fig. 6(*a*), while those causing a blue shift in the same system and stabilizing it (L-xylose, D-fructose, D-galactose, D-mannose, D-arabinose, L-fucose and L-glucose) fit a linear plot in Fig. 6(*b*). A remarkable correlation between monolayer property and molecular structure is observed: the smaller the angle α between two intramolecular cholesterol moieties, the lower is the transition pressure. The monolayers of complexes with a small waterfacing angle α such as the glucose complex require a lower surface pressure to achieve phase transition and to rearrange both the structure of the complex and packing in the monolayer compared with complexes of larger angle α, *e.g.* with fructose. *Vice versa*, the energy required for rearranging the molecular structure is higher, if the Ph–Ph dihedral angle, which is the complement to 180° of α, is already small. This fact can be understood on the basis of common structural models. Alternatively, we also tried to correlate the transition pressure with the angle for the complexes with furanose-type monosaccharides with the boron atom sp^3-hybridized,* because in aqueous bulk solution monosaccharides adopt this form in boric acid complexes.[30] The waterfacing angles of these complexes are included in Table 2 for the energetically most favoured complex structures. The angles are different from that of pyranoses. However, there is no correlation between transition pressure and waterfacing angle for the furanose complexes. The difference in correlation suggests that the pyranose form is predominant under the experimental conditions and that the monolayer provides an environment different from aqueous bulk solution, where the furanose form predominates. This finding is in agreement with the previously proposed reduced solvating capability of water molecules near the air–water interface.[32]

When the temperature is increased from 293 to 303 K, the phase transition occurs at lower surface pressure. This is contrary to the monolayer behaviour of simple fatty acids and other amphiphiles like cholesterol, where the transition in compressibility occurs at higher surface pressure in case of higher temperature.[20b,33] However, there is a significant difference between the two systems: only physical quantities of the monolayer forming pure amphiphiles depend on the temperature, while temperature-dependent chemical equilibria overlap with the change of the physical properties in case of the boronic acid complexes. From the thermodynamic point of view it is clear, that the rearrangement of the chemical structure of the complexes requires a smaller energy contribution ΔG from the compression if the energy contribution from the reaction temperature is higher.

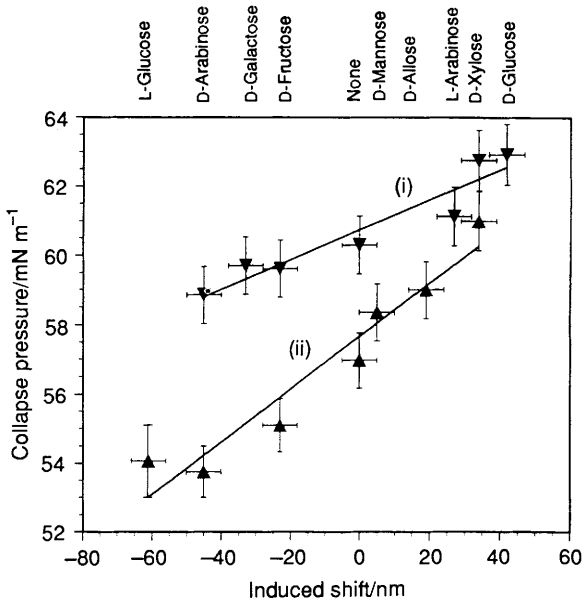

Fig. 7 Collapse pressure of monolayers of **1** at 293 and 303 K in the presence of monosaccharides plotted *vs.* the shift of the reflectance maximum in the cholesteric liquid crystal system (measured at 300 K) induced by complexing **1** with those monosaccharides. This shift is linearly correlated with the Ph–Ph angle. ▼, 293 K; ▲, 303 K. R = (i) 0.93, (ii) 0.91.

The collapse pressure of monolayers of **1** in the presence of monosaccharides is plotted *versus* the shift in the reflection maximum induced by 1.2 mol% of complexes of **1** with those monosaccharides in the cholesteryl chloride, nanoate composite liquid crystal[1] at 300 K in Fig. 7. This spectral shift is linearly related to the Ph–Ph dihedral angle and is used instead of α in order to conveniently distinguish between optical isomers. Despite the high surface pressure it was possible to observe a reproducible trend under the same experimental conditions. The plot clearly shows that optical isomers of monosaccharides influence the monolayer to a different extent. The discrimination of optical isomers results from the chirality of the cholesterol moiety. The complex involving a D-isomer of monosaccharide is the diastereoisomer of the complexed L-isomer, so that the packing of these complexes in the compressed monolayer is different and causes different collapse pressures. In order to underline this fact, we estimated the limiting area after phase transition of **1** in the presence of 11 mmol dm^{-3} monosaccharides. In Fig. 8 the limiting area is plotted *versus* the induced shift as a measure of chirality. Similar to Fig. 7, chiral discrimination is observed but also a difference between the complexes which cause a blue and a red shift in the liquid crystal system, respectively. Since the limiting area was found to be almost independent of the compression speed in contrast to the collapse pressure, kinetic effects can be excluded as a reason for the different impact of optical isomers. Thus, it is concluded that the chiral discrimination of monosaccharides by **1** due to a different crystal structure observed in the liquid-crystal system is retained in its monolayer due to different packing.

In conclusion, the present paper demonstrated that steroidal boronic acid **1** has potential to detect monosaccharides at the air–water interface. The absolute configuration and the monolayer stability can be correlated through the Ph–Ph dihedral angle of the 1 : 2 monosaccharide–**1** complexes. It was found that the monosaccharides are pyranoses in the complexes at the air–water interface. The chiral discrimination of monosaccharides

* Supplementary material (calculated structures and energies) is available upon request directly from the authors.

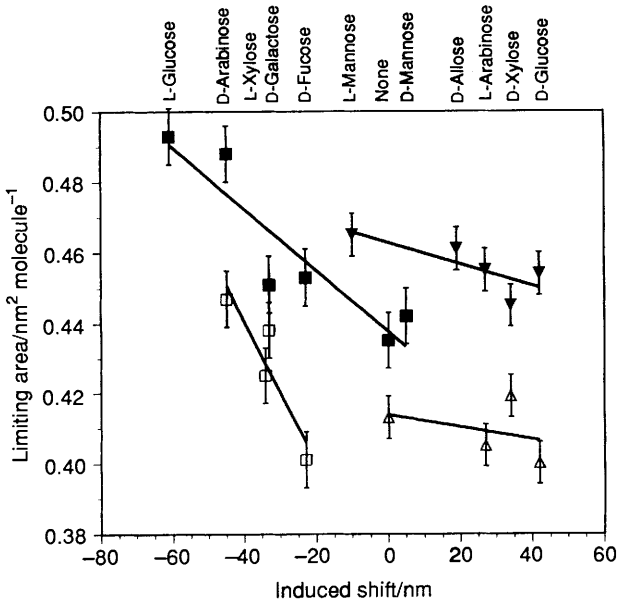

Fig. 8 Extrapolated limiting molecular area of **1** in the presence of 11 mmol dm^{-3} of monosaccharides at 293 and 303 K after phase transition, plotted *vs.* the induced shift in the cholesteric liquid crystal system. ■, Blue shift, 303 K; □, blue shift, 293 K; ▼, red shift, 303 K; △, red shift, 293 K.

in the liquid-crystal system is reproduced in the monolayer system due to the differences in the surface structure. We believe that this finding should be utilized as a novel monosaccharide sensing system.

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