



to a transient, replication process demands a quasi-unlimited reservoir, or else a

how environments react by self-organization to being kept far from equilibrium.

environment 'makes use' of the system; now, we would adopt the conventional way of referring to the *system* by stating that it requires and processes energy from

the environment in order to live.



a chemical environment leading to a genetic system is, in principle, equally valid

for an emergence of autocatalytic metabolic cycles. A teleomatically driven self-

organization within a chemical environment could, in principle, take a course

may come across molecular structures which reveal themselves as candidates for

having been intermediates (if there were any) along the evolutionary path toward

the biomolecule we know today.

Obviously, the choice of the alternative's structure is crucial. In choosing it, one draws from the wealth of experience about the reactivity and synthesis of organic

molecules, as well as from the findings and concepts of prebiotic chemistry (Miller

and the 3'-deoxy-allopyranosyl systems (Hammer *et al.*, 1992), it can be argued

convincingly that the reason for this divergence is intrastrand steric hindrance in the pairing conformation. The three examined  $(\text{CH}_2\text{O})_6$  hexopyranose sugars

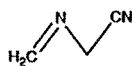
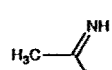
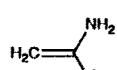
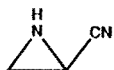
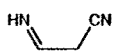
(and, foreseeably, also the five remaining diastereomers) are too bulky to serve

as building blocks of efficient pairing systems. The short answer to the question

'Why pentose, and not hexose nucleic acids?' that emerges from these studies











[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

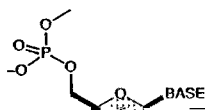
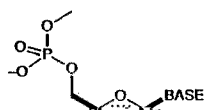
[REDACTED]

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# Thermodynamic Data of Homo-DNA(=dd)- and DNA(=d)-Oligonucleotide Duplexation

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HOMO - DNA :

PURINE - PURINE PAIRING

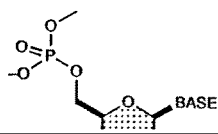
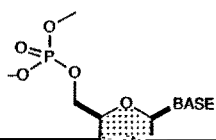
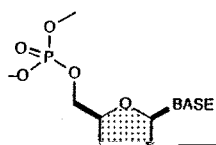
MELTING TEMPERATURES (°C) OF HEXAMER - DUPLEXES:

10mM Tris pH 7

| A | H | D | X | I | G |

dd-BBBBBB  
BBBBBB-dd

dg-BBBBBB



ALLOSE-NA:

GUANINE-CYTOSINE PAIRING

H (%)

<sup>24</sup>allo(GC)<sub>5</sub>

H (%)

<sup>24</sup>allo(G=C<sub>5</sub>)

100

**Tm**

10  $\mu$ M Oligomer  
150 mM NaCl, 10 mM buffer

pH 7

pH 4.3

(c ~10 $\mu$ M, 0.15 M NaCl, pH 7, 260nm)

2',3'-DIDEOXY-ALLO-

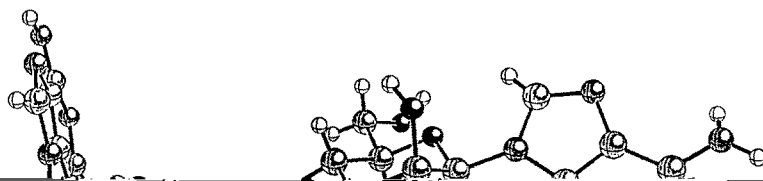
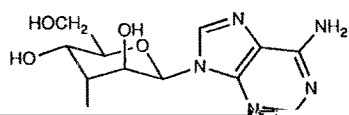
ALLO-

ALTROSE-NA:

ADENINE-URACIL PAIRING

Alt([A-U]<sub>6</sub>)

Alt (A<sub>5</sub>-U<sub>5</sub>)



## Why Pentose and not Hexose Nucleic Acids?

Conclusions (preliminary)  
based on experimental observations on Gluco-, Allo- and

Altropyranosyl-(6' → 4')-oligonucleotides:

Hexopyranosyl-(6' → 4')-oligonucleotide analogues of RNA

derived from (CH<sub>2</sub>O)<sub>6</sub>-hexoses are pairing systems drastically

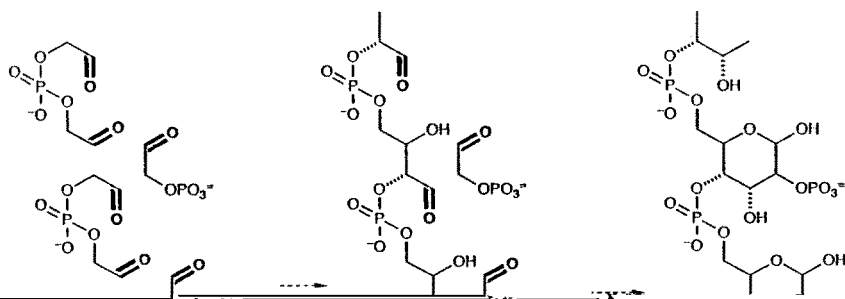


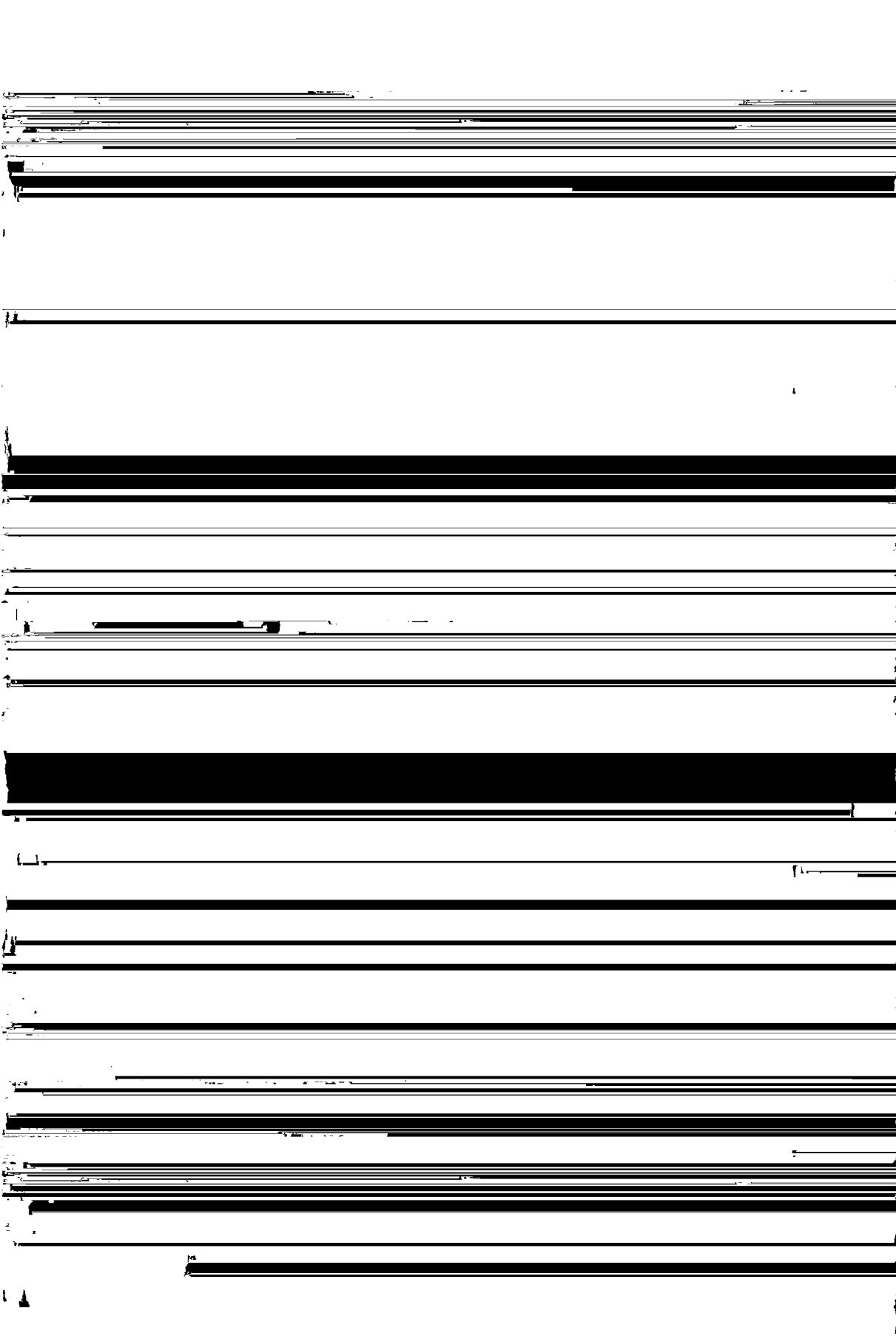
ALLO-(4'→6')  
g/g

ALLO-(2'→6')  
g/t

### Oligonucleotide Backbones by Aldomerization:

#### Retrosynthetic analysis for HFXO-pyransyl-(4'→6')-oligonucleotide backbones



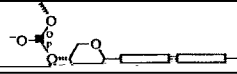


# $\beta$ -BIRD-PYRANOSYL (2' $\rightarrow$ 3') OLIGONUCLEOTIDES

## ("PYRANOSYL - RNA")

### Pairing Conformation of Backbone

( hypothetical )



10/10/10

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

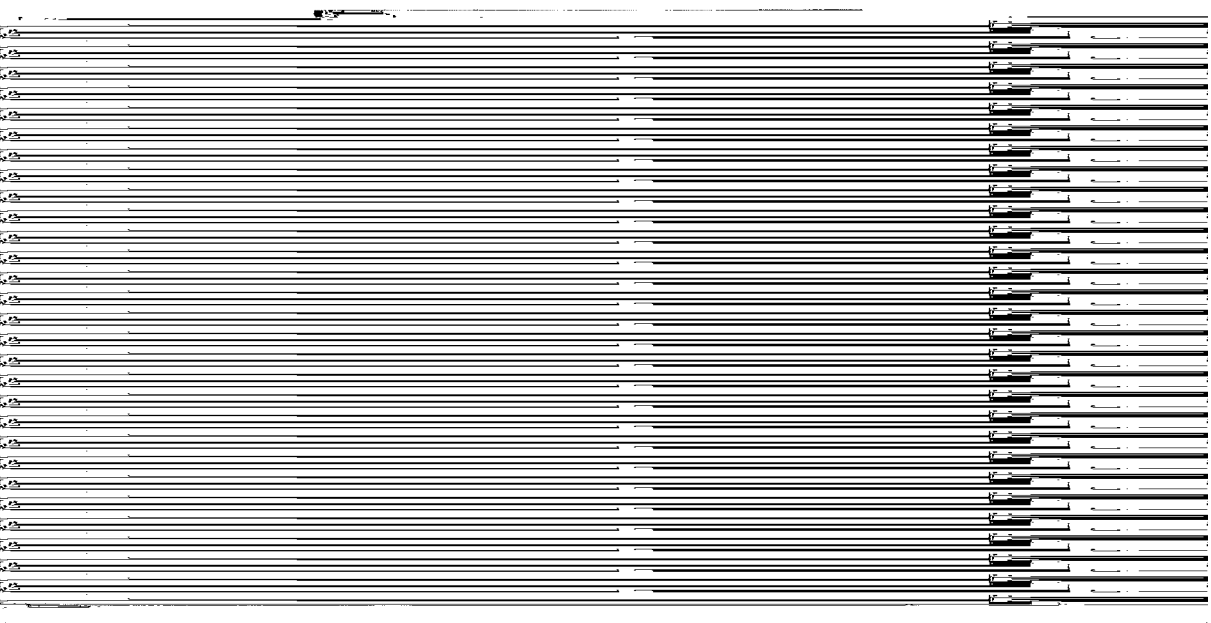
[REDACTED]

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[REDACTED]

[REDACTED]

[REDACTED]

Mixing-curve of p-Ribo(A<sub>8</sub>) + p-Ribo(U<sub>8</sub>)

Hyperchromicity (%)

## Thermodynamic Data of Ribopyranosyl-(4'→2')-oligonucleotides



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Dearhead, S., Foggia, J. P., and Eschenmoser, A.: 1999, 'Chemistry of  $\alpha$ -Aminoacids', *Angew. Chem.* **111**, 1033-1034.

2-cyanoacrylate: Photochemical Formation from 2-Aminononenenitrile' *Helv. Chim. Acta* **72**, 1033-1034.

