ELSEVIER

Journal of Molecular Structure (Theochem) 505 (2000) 149–159

THEO CHEM

www.elsevier.nl/locate/theochem

Self-associative base-pairing in some nitrogen heterocycles: a PM3 SCF-MO study

D.M.L. Buam, R.H.D. Lyngdoh*

Department of Chemistry, North-Eastern Hill University, Bhagyakul, Shillong, 793003, India

Received 18 January 1999; received in revised form 8 May 1999; accepted 14 September 1999

Abstract

Self-associative hydrogen-bonded pairs arising from a substituted pyrrole, a substituted imidazole, substituted pyridines, pyrimidines and pyrazines are studied using the semiempirical PM3 SCF-MO method. The search for a set of self-associative base-pairs mimicking the characteristics and functionality of DNA bases led to the identification of three imidazole pairs as possible candidates. Pairs with oxygen rather than fluorine as the electronegative atom are in general more stable. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Hydrogen bonding; Nitrogen heterocycles; PM3 SCF-MO method; Self-association

1. Introduction

Hydrogen-bonding is well-known as the basis for self-associative dimer formation in a large number of organic molecules, e.g. in carboxylic acid dimers in the gas phase. The essential structural requirement is the presence of a covalent A–H bond and of a B atom on the same molecule, where A and B are first row electronegative atoms like nitrogen, oxygen or fluorine. This study focuses on the ability of various nitrogen heterocycles to undergo pairing with themselves. Self-associated hydrogen-bonded dimer pairs may be contrasted with pairs involving two different molecules (hetero-associative pairs). The latter type of hydrogen-bonded association is also well-known, forming the basis for molecular recognition in the world of biology, as the Watson–Crick base pairs of DNA exemplify.

While the base pairs of DNA are characterised by the unique ability of each base to pair only with the appropriate complementary base (within the limits imposed by the configurational constraint), self-associative pairs cannot be described as complementary nor serve the function of molecular recognition in the manner of DNA bases. Self-recognition is the keyword here, and any replication of a macromolecule of this type by a hydrogen-bonded process would result in an identical copy of the original. In DNA, each strand when replicated gives rise to a copy of the *opposite* or complementary strand, not of itself.

The aim here is to design putative molecules which can recognise themselves in a non-ambiguous fashion by hydrogen-bonding, which could then pave the way for the design and construction of macromolecules which assume their structure and replicate by self-recognition and self-association rather than complementary pairing. Such macromolecules would consist of a sequence of hydrogen-bonded dimeric pairs linked together by some sort of a backbone, the details of which are yet to be designed. Perhaps a sugar-phosphate backbone as in DNA would function well here, which means that the base residues in the

* Corresponding author.

PII: S0166-1280(99)00344-9

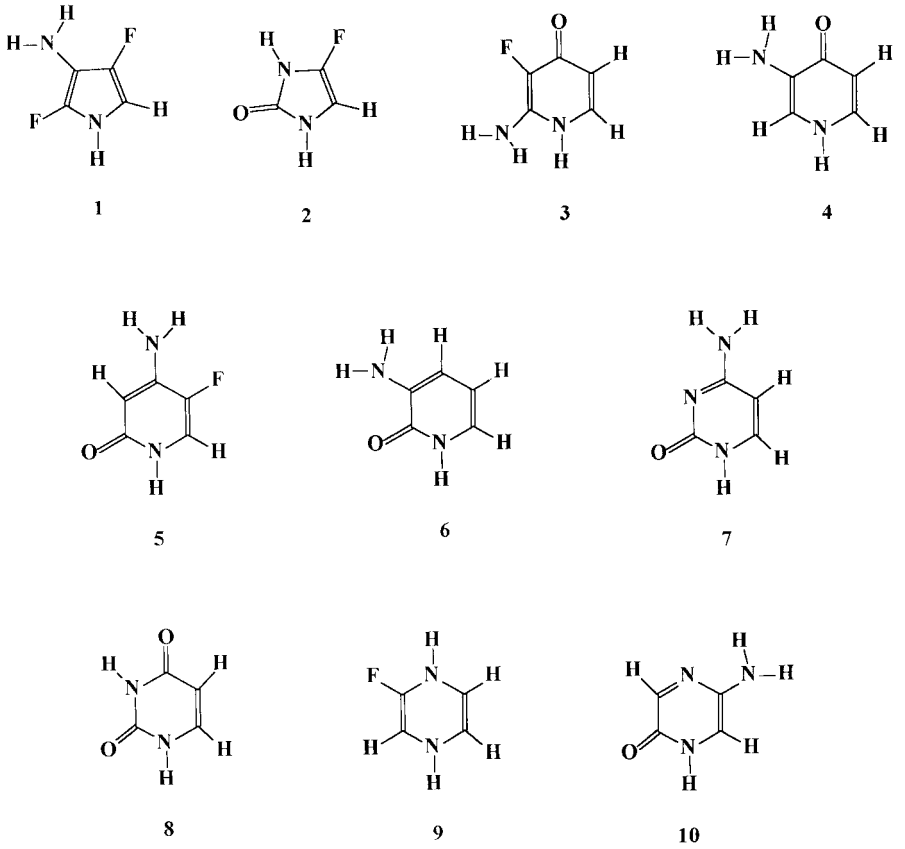

Fig. 1. The monomeric structures for **1** (2,4-difluoro-3-aminopyrrole), **2** (4-fluoroimidazol-2-one), **3** (2-amino-3-fluoropyrid-4-one), **4** (3-amino-pyrid-4-one), **5** (4-amino-5-fluoropyrid-2-one), **6** (3-aminopyrid-2-one), **7** (4-aminopyrimid-2-one), **8** (4-oxo-pyrimid-2-one), **9** (1,4-dihydro-3-fluoropyrazine), **10** (5-aminopyraz-2-one).

macromolecule would exist in the form of their *N*-glycosides.

Hydrogen-bonded base pairing of nucleic acid bases has been widely studied experimentally and theoretically. The 29 different base-pairs arising from DNA bases have been discussed [1] and subjected to theoretical investigation [2]. Both self-associative and hetero-associative pairs have been considered [3,4]. The various contributory factors to duplex formation have been discussed [5], and include $\pi-\pi$ stacking interactions [6]. Self-associative pairs involving deoxyribonucleotides were studied [7] with respect to the kinetics and thermodynamics of duplex formation. The pairing properties of chemically modified DNA bases have also been studied theoretically [8,9]. Hydrogen bonding and stacking interactions have been studied for DNA base-pairs using high level theory [10]. Novel nucleic acid bases and their pairing properties have been theoretically studied [11]. The possibility of non-planarity in DNA bases has been treated by high-level theory [12]. Other theoretical studies include base-pair interactions [13], strengths of hydrogen bonds [14], and possibility for mutagenesis in base-pairs through proton transfer [15] or proton tunnelling.

Three factors enter into play in determining the structure, stability and function of such information-bearing macromolecules. The first is the configuration of the hydrogen-bonded pairs, which perhaps, as in DNA, plays a primary role in deciding secondary structure and stability of the macromolecule. The second factor is the role of stacking interactions,

Table 1
PM3 data for hydrogen bonding of self associated base pairs from 2,4-difluoro-3-amino pyrrole

System	E_p	H-bond	R_{hb}	R_{ab}	H-bond angle	θ_{hb}
A type						
11	−2.088	H1–F2	1.811	2.643	∠NHF	159.91
		F2–H1	1.805	2.623	∠FHN	154.87
B-type						
12	−1.929	H1–F2	1.804	2.715	∠NHF	147.53
		F2–H3	1.857	2.708	∠FHN	136.45
13	−2.025	H1–F4	1.996	2.884	∠NHF	149.90
		F2–H3	2.026	3.039	∠FHN	152.28
14	−1.520	H1–F4	2.028	2.902	∠NHF	154.87
		F2–H5	2.198	3.795	∠FHC	138.72
C Type						
15	−1.514	H3–F2	1.816	2.800	∠NHF	167.73
		F2–H3	1.813	2.807	∠FHN	172.01
16	−1.276	H3–F4	1.785	2.570	∠NHF	137.18
		F2–H5	2.201	2.914	∠FHC	118.68
17	−2.579	F4–H3	1.777	2.784	∠FHN	159.79
		H3–F4	1.815	2.732	∠NHF	165.29
18	−1.511	F4–H5	2.210	3.043	∠FHC	143.10
		H3–F4	1.927	2.804	∠NHF	130.35
19	−0.712	F4–H5	2.230	3.419	∠CHF	142.64
		H5–F4	2.305	3.228	∠FHC	138.53
20	−2.107	F4–H5	1.912	2.908	∠NHF	173.75
		H5–F4	1.893	2.868	∠FHN	164.06

while a third factor is the flexibility of the backbone. We shall for the time being assume that the first factor of base-pair configuration is the main one, and therefore consider only the free bases and their pairs in this preliminary study.

Four sets of molecules have been chosen here for study, which are depicted in Fig. 1. These are (1) the five-membered ring system 2,4-difluoro-3-aminopyrrole **1**, (2) the five-membered 4-fluoro-imidazol-2-one **2**, (3) four different substituted pyridones, viz. 2-amino-3-fluoropyrid-4-one **3**, 3-aminopyrid-4-one **4**, 4-amino-5-fluoropyrid-2-one **5**, and 3-aminopyrid-2-one **6**, and (4) a set of four different six-membered nitrogeneous bases, viz. 4-aminopyrimid-2-one **7**, 4-oxopyrimid-2-one **8**, 1,4-dihydro-3-fluoropyrazine **9** and 5-aminopyraz-2-one **10**.

These various pairs are considered with a view to designing a set of bases which could be used as building blocks for duplex macromolecules which replicate by self-association yielding a copy identical with the original. Such a set may be characterised by the following features:

1. Subject to the given configuration, each base on a strand can pair only with itself on the opposite strand, so that the formation of base-pairs is non-ambiguous and specific.
2. All four self-associative pairs possess almost the same basic configuration so as to allow for a uniformity of duplex structure throughout, regardless of base sequence.
3. The configuration should allow for reversibility of the base pair, so that the duplex is not one-sided. This means that the configuration markers should have values such that when the base pair is reversed, the configuration remains the same.
4. The base-pairs should possess an appreciable pairing energy to ensure sufficient stability of the duplex.

For the purpose of this study, a set of bases possessing the above four characteristics is termed as a "DNA-type set".

The hydrogen bonds here are of the form A–H···B or A···H–B. Facility of hydrogen-bonded base-pairing is represented by E_p, the enthalpy of pairing in

Table 2
Configurational data for C-type pairs from 2,4-difluoro-3-amino-pyrrole

System	R_{nn}	θ_1	θ_2	ϕ_{nh}	E_P
15	7.272	116.76	116.78	178.85	−1.514
16	6.632	105.31	88.77	−5.40	−1.276
17	9.092	173.07	169.79	158.96	−2.579
18	7.922	158.18	113.09	1.91	−1.511
19	7.103	127.02	125.57	−179.94	−0.712
20	8.037	173.63	105.51	117.57	−2.107

kcal/mol. Features of note to study with regard to the hydrogen bonds formed include: (a) the actual length R_{hb} of the hydrogen bond (the H···B or A···H distance), (b) the overall distance R_{ab} between the two electronegative atoms A and B, and (c) the angle θ_{hb} of the hydrogen-bond.

All the above systems were studied bearing in mind the possibility of *N*-glycoside formation, so that one ring nitrogen atom has to be left free for *N*-glycoside formation. Apart from the thermodynamic feasibility of dimerisation, the configuration of the base pair formed is also taken note of. Configurational markers were used to define the configuration of the dimer, which include: (a) R_{nn}, the distance between the two glycoside-bonded nitrogens, (b) ϑ_1 and ϑ_2, the angles between the two glycosidic bonds and the N–N vector traversing the two constituent bases, and (c) ϕ_{nh}, the dihedral angle between the two glycoside bonds. Since the actual glycosides are not explicitly used here, careful note has to be taken of the nitrogen atoms, which serve to form one terminus of the glycosidic bond to be. All such nitrogens in the free bases must be covalently bonded to a hydrogen, so that this N–H bond can serve to model the would-be glycosidic linkage. In the figures portraying the configurations of the base-pairs, the would-be glycosidic linkage is represented by a pointed arrow.

2. Theoretical methodology

All the monomers of Fig. 1 and the resultant self-associative pairs were subjected to molecular orbital calculation using the semiempirical PM3 SCF-MO method [16] of the MOPAC package. This method is particularly suited to studying hydrogen bonding in nitrogeneous heterocycles like DNA bases [17]. Full optimisation of molecular geometry was carried out without any symmetry constraints using the Davidon–Fletcher–Powell algorithm [18,19]. The

Table 3
PM3 data for 10 unique hydrogen bonded dimers of 4-fluoroimidazol-2-one

System	E_p	H-bond	R_{ab}	R_{hb}	H-bond angle	θ_{hb}
21	−7.293	O2–H3	2.782	1.791	∠OHN	164.70
		H3–O2	2.783	1.791	∠NHO	164.70
22	−2.880	O2–H3	2.808	1.789	∠OHN	160.27
		H3–F4	3.029	1.971	∠NHF	166.34
23	−0.917	H3–F4	2.770	1.804	∠NHF	159.94
		F4–H3	2.775	1.806	∠FHN	160.63
24, **31**, **34**, **33**	−0.328	F4–H5	2.887	2.131	∠FHC	141.76
		H5–F4	2.888	1.995	∠CHF	147.67
25, **27**	−3.774	O2–H5	2.886	1.802	∠OHC	162.59
		H3–F4	2.894	1.812	∠NHF	168.79
26, **30**	−1.146	H3–F4	2.862	1.960	∠NHF	152.14
		F4–H5	3.034	2.102	∠FHC	160.63
28	−7.136	O2–H1	2.785	1.790	∠OHN	164.91
		H3–O2	2.782	1.787	∠NHO	166.44
29	−2.422	H3–O2	2.737	1.798	∠NHO	149.53
		F4–H1	2.692	1.798	∠FHN	142.92
35	−7.530	H1–O2	2.790	1.795	∠NHO	166.86
		O2–H1	2.791	1.793	∠OHN	167.09
32, **36**	−4.456	H1–F4	2.800	1.798	∠NHF	173.14
		O2–H5	3.045	1.987	∠OHC	159.36

Table 4
Configurational data for 4-fluoroimidazol-2-one pairs

System	R_{nn}	θ_1	θ_2	ϕ_{nh}	E_P
N1:N1 type					
21	6.768	127.18	126.30	177.67	−7.290
22	7.332	156.29	120.75	−61.13	−2.880
23	7.937	155.08	160.53	157.43	−0.917
24	6.250	120.59	119.57	176.87	−0.328
25	6.897	131.76	130.39	−11.44	−3.770
26	7.453	149.20	121.82	−77.03	−1.146
N1:N3 and N3:N1 types					
27	6.314	113.63	106.29	164.58	−3.770
28	6.781	129.97	126.50	171.33	−7.136
29	7.171	121.36	163.39	−52.30	−2.422
30	7.614	155.37	113.93	51.37	−1.146
31	6.444	119.73	114.29	−4.89	−0.328
32	6.408	106.63	116.85	34.92	−4.456
33	6.839	124.79	124.86	−6.70	−0.328
N3:N3 type					
34	6.454	124.17	123.94	177.89	−0.328
35	6.768	126.74	127.83	174.64	−7.530
36	6.885	131.54	130.22	−157.59	−4.456

optimised geometries and minimised energies thus obtained provided the basis for the results discussed here.

3. Results and discussion

Table 1 presents the H-bond data on the 10 different dimers obtained for 2,4-difluoro-3-aminopyrrole **1**, while Table 2 gives the configurational data for six of these pairs which allow for glycosidic linkages on both monomers. Table 3 furnishes the H-bond data for the 10 unique pairs obtained from 4-fluoroimidazol-2-one **2**, while Table 4 lists the configurational data for the 15 different pairing configurations which can be derived from these 10 pairs. Table 5 gives the H-bond data for the four different dimeric pyridone pairs obtained from **3**, **4**, **5** and **6**, with Table 6 providing the configurational data for these. Table 7 presents the H-bond data for the four six-membered ring pairs built up from **7**, **8**, **9**, and **10**, while Table 8 furnishes their configurational data.

Table 6
Configurational data for four pyridone pairs

System	R_{nn}	θ_1	θ_2	ϕ_{nh}	E_p
37	8.140	117.83	115.71	177.55	−3.793
38	9.865	165.35	164.68	175.65	−2.392
39	9.746	148.90	154.83	−170.58	−1.275
40	7.297	99.88	104.00	−177.27	−4.118

3.1. Self-association of 2,4-difluoro-3-aminopyrrole

The 10 pairs studied here exhaust all pairing possibilities subject to the condition of essential coplanarity. The monomer itself is a largely planar aromatic system. The 10 pairs are classified into three types (Table 1). The first (Type A) is characterised by no possibility of *N*-glycoside formation, and includes the pair **11**. The second (Type B) allows for only one *N*-glycosidic bond, and includes the pairs **12**, **13**, and **14**. The third group (Type C) requires the existence of two glycosidic linkages, and include the pairs **15**, **16**, **17**, **18**, **19** and **20** (Fig. 2). Only Type C pairs can lend themselves to the possibility of macropolymeric duplex formation. Since only one type of monomer is considered here, the only kind of polymer formed would have to be homopolymeric.

The H-bond data of Table 1 reveals a relationship

Table 5
PM3 hydrogen-bond data for four pyridone pairs

System	E_p	H-bond	R_{hb}	R_{ab}	H-bond angle	θ_{hb}
37	−3.793	F3–H2	1.805	2.785	∠FHN	177.25
		H2–F3	1.824	2.666	∠NHF	174.99
38	−2.392	O4–H5	2.007	2.910	∠OHN	170.67
		H5–O4	1.926	3.024	∠NHO	165.30
39	−1.275	F5–H4	1.917	2.781	∠FHN	165.41
		H4–F5	1.909	2.992	∠NHF	176.54
40	−4.118	O2–H3	1.991	2.653	∠OHN	168.13
		H3–O2	1.952	2.688	∠NHO	174.89

Table 7
PM3 hydrogen-bond data for the pyrimidine, pyrazine pairs

System	E_p	H-bond	R_{hb}	R_{ab}	H-bond angle	θ_{hb}
41	−0.958	N3–H4	1.993	2.753	∠NHN	165.62
		H4–N5	1.973	2.770	∠NHN	166.44
42	−2.417	O3–H4	2.009	2.956	∠NHO	162.12
		H3–O4	1.837	2.837	∠OHN	166.18
43	−1.269	H4–F5	1.794	2.945	∠NHF	159.22
		F5–H4	1.802	2.972	∠FHN	173.19
44	−0.681	N4–H5	1.994	2.870	∠NHN	159.22
		H5–N4	1.976	2.942	∠NHN	165.98

between the magnitude of the pairing energy E_p and the types of hydrogen bonds present in the pair. The pair **17** displays the largest E_p value (−2.579 kcal/mol) and involves two strong N–H···F bonds which are fairly linear. The pairs **11**, **12**, **13** and **20** also possess fairly large pairing energies (from −2.025 to −2.107 kcal/mol), having two N–H···F bonds, which are less linear for **11** and **13**. Smaller E_p values are given by the pairs **14**, **16** and **18**, which are concomitant with the presence of one weak C–H···F bond along with one stronger N–H···F bond. The pair **15** displays an E_p value smaller than expected for its two fairly linear N–H···F bonds. The C–H···F hydrogen bond lengths R_{hb} are observed to be somewhat longer than for N–H···F hydrogen bonds, ranging from 2.198 to 2.210 Å. The pair **19** is characterised by the smallest E_p value of this set (−0.712 kcal/mol), which may be explained by the presence of two weak and long C–H···F bonds which deviate from linearity quite appreciably.

Of all these pairs, only the Type C pairs **15** to **20** give scope for duplex formation. Their configurational data is given in Table 2. Each pair presents its own unique configuration different from the rest, so that the possibility of constructing a DNA-type set of bases does not arise. Pairs **15**, **16**, **18** and **19** are quite coplanar, as evinced from their ϕ_{nh} values, while pairs **17** and **20** deviate appreciably from coplanarity. The stability of the various duplexes thus formed might be expected to be directly related to their E_p values. The overall stability would also include the additive effect of having a long sequence of base-pairs that allows for cooperative interactions. Note that the R_{nn} values are largest for the most stable pair **17**, and that the order of magnitude for E_p with respect to the pair is **17** > **20** > **18** > **16**, running parallel to the order for the R_{nn} values. This could indicate some effect of looseness of pair-packing upon pairing facility.

3.2. Self-association of 4-fluoroimidazol-2-one

Table 3 gives the hydrogen-bond data for the 10 unique dimeric pairs arising from **2**. All these allow for two *N*-glycosidic linkages and duplex formation. Depending upon which nitrogens are considered as termini of the glycosidic bonds, these 10 pairs may be accommodated into 16 different configurations. These 16 configurations are classified into three groups based on which nitrogens are considered for glycosidic bond formation (see Table 4). The monomer **2** has two nitrogen atoms available for *N*-glycosylation, viz. the N1-atom and the N3-atom. The first group involves the N1 atoms of both the monomers for *N*-glycosylation, hence the term N1–N1 (Fig. 3). The second group accordingly has an N1–N3 or N3–N1 type of basic configuration, while the third group has the N3–N3 type of alignment.

Here again, strength of hydrogen bonding as given by the E_p index is seen to depend largely upon the type and linearity of the involved hydrogen bonds. The strongest bonding is observed for those pairs which possess two H-bonds of the N···H–O type, with electronegative nitrogen and oxygen atoms on the two

Table 8
Configurational data for the pyrimidine, pyrazine pairs

System	R_{nn}	θ_1	θ_2	ϕ_{nh}	E_p
41	8.442	158.09	161.06	165.00	−0.958
42	8.775	154.83	158.05	175.77	−2.417
43	8.809	162.10	165.81	−150.40	−1.269
44	8.371	167.29	164.74	173.78	−0.681

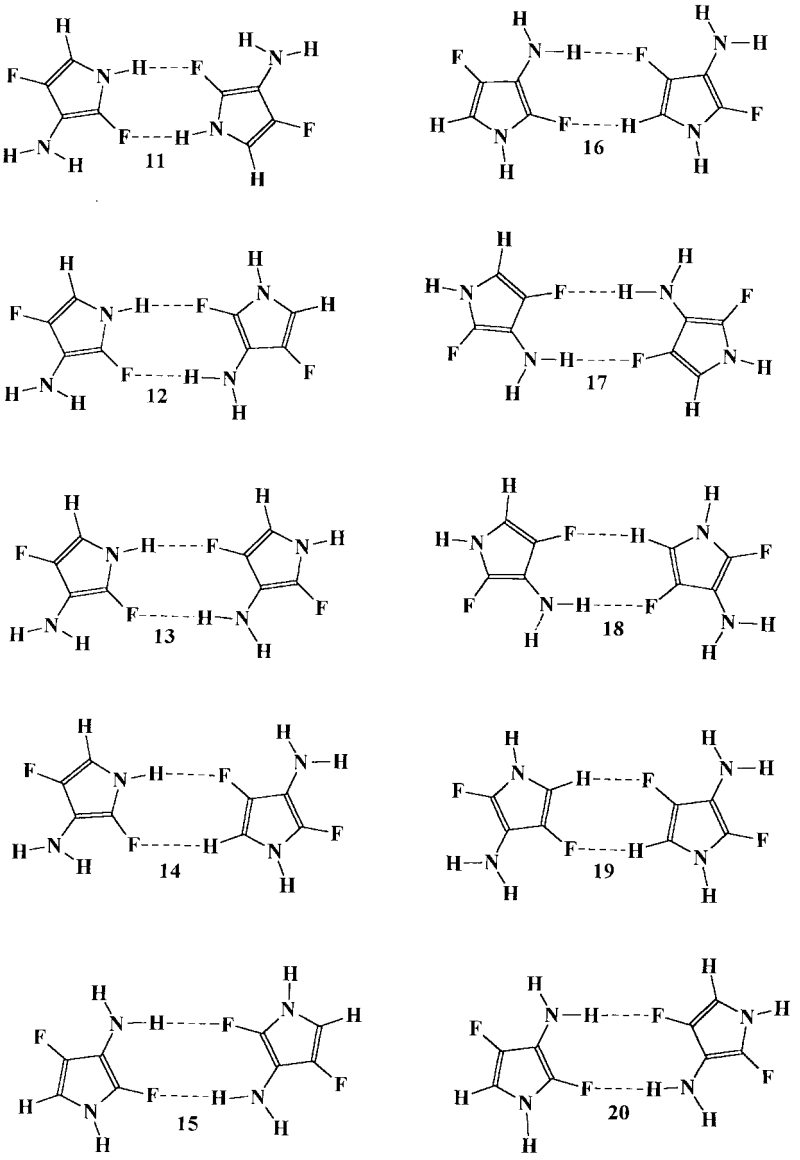

Fig. 2. Configurational structures for self associative dimers of 2,4-difluoro-3-aminopyrrole.

sides. The largest pairing energies in this set are −7.293, −7.136 and −7.530 kcal/mol for systems **21**, **28**, and **35**, respectively, which E_p values are appreciably larger than the most stable pyrrole pairs of Table 1. Of these, system **35** has H-bond angles closest to 180° (166.86 and 168.79°), which explains its large pairing energy. Systems which have an O···H–N bond and an N–H···F bond together (as typified by systems **22** and **29**) display somewhat smaller pairing energies. An unexpectedly small pairing energy of −0.917 kcal/mol is predicted for system **23** with two N–H···F H-bonds, undoubtedly attributable to the non-linear H-bond angle of 159°. In the case of six-membered ring systems, we might expect larger pairing energies and H-bond angles closer to 180°. It may be concluded that five-membered rings

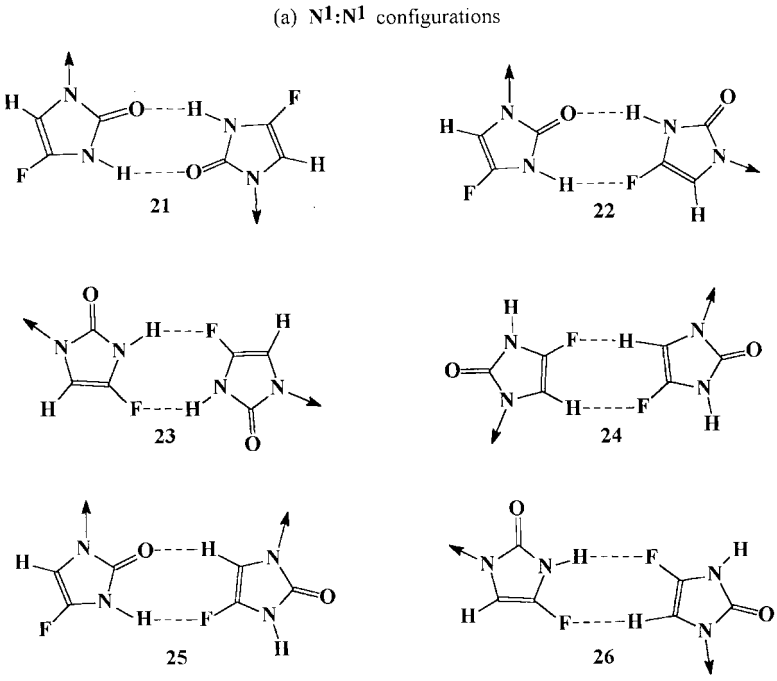

Fig. 3. Sixteen different configurations from 4-fluoroimidazol-2-one pairs.

can impose some geometrical constraints to feasibility of H-bonding through departure from linearity.

Pairs containing C–H···F type H-bonds possess small pairing energies. For systems **26** and **30** (−1.146 kcal/mol) and the systems **24**, **31**, **32**, and **34** (−0.328 kcal/mol), these small values may be linked to H-bond angles of 152.14 and 160.63° for the former set and H-bond angles of 141.76 and 141.67° for the second set. Pairs with one C–H···O type of H-bond are predicted to have larger pairing energies viz. the pairs **25** and **27** (−3.774 kcal/mol) and the pairs **32** and **36** (−4.456 kcal/mol). This may be attributed to a straightening of the F···H–N H-bond angle (162.59° for **25** and **27** and 173.14° for **32** and **36**) which facilitates H-bonding.

Out of all these pairs, it is seen that only the pairs **21**, **28** and **35** are characterised by the criteria for mimicking the DNA-type bases. The pairing energy is substantial in all three cases (−7.136 to −7.530 kcal/mol). The configurations are similar, as evinced by the R_{nn} values of 6.768–6.781 Å, by the values of the dihedral ϕ_{nh} close to 180°, as well as the ϑ_1 and ϑ_2 values of 126.30–129.97°. The ϑ_1 and ϑ_2 markers for each pair are almost equal in value, pointing to reversibility of each base-pair. Since the monomer for the three pairs is the same, the informational content of the putative duplex macromolecule arising from these pairs is linked not to the identity of the base, but rather to the topology and steric arrangement of the pairs, which is different for each case. One drawback is that instead of four base-pairs, we have here only three which could thus lead to a triplet coding dictionary of only 3^3 or 27 code words.

3.3. Pyridone base-pairs

These pairs are governed by the sole constraint that the ring nitrogen heteroatom be left free for formation of an *N*-glycosidic bond (see Fig. 4). The H-bond data for the four pyridone pairs **37**, **38**, **39** and **40** are given in Table 5. The hydrogen bonds here are quite linear, much more so than was the case for the pyrrole and imidazole pairs studied earlier. This is a result of the sp^2 hybridised six-membered pyridone ring system, which allows for each pair of hydrogen bonds to

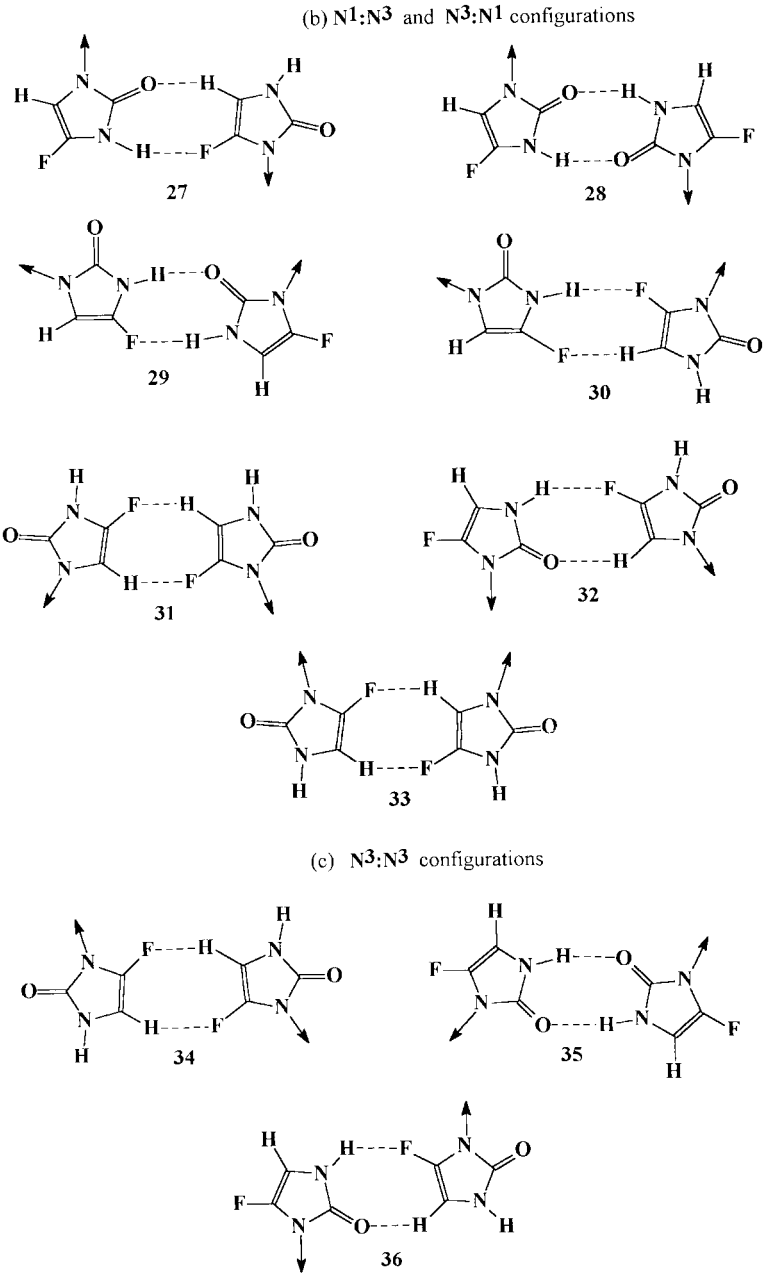

Fig. 3. (*continued*)

occur within the outline of a hexagon, as may be seen from Fig. 4.

All these pairs are quite feasible thermodynamically, with E_p ranging from −1.275 to −4.116 kcal/mol. The most stable pair **40** is formed through hydrogen bonds involving oxygen, while the least stable pair **39** incorporates fluorine in the hydrogen bonds.

Each pair is characterised by its own individual configuration as given in Table 6. This rules out the

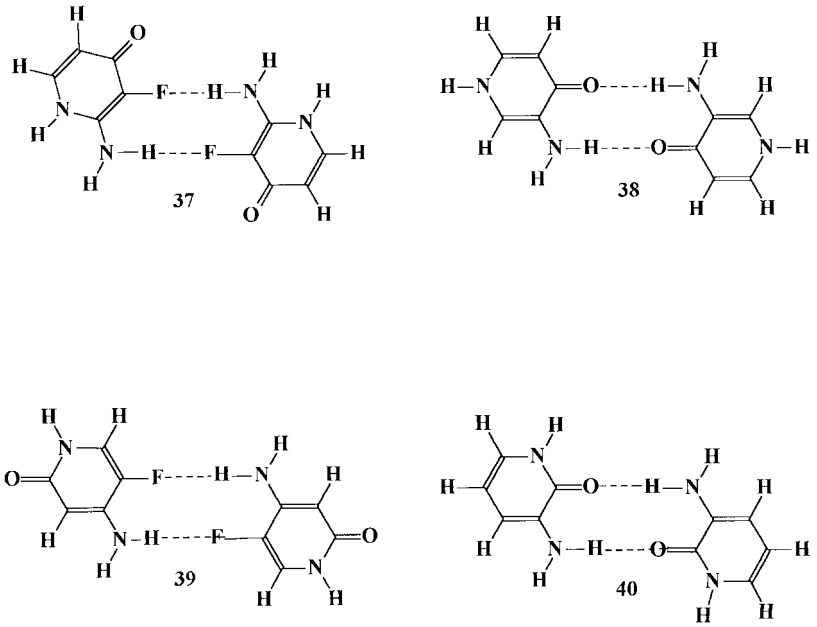

Fig. 4. Self associative pairs for the four pyridones.

possibility for formation of a DNA-type set of bases. The pairs are all of the reversible type, since in each case the ϑ_1 and ϑ_2 markers are of approximately equal value. These pairs are also quite planar, as seen from the ϕ_{nh} values (all near 180°).

3.4. Pyrimidine and pyrazine pairs

Here again, base-pairing is governed by the sole condition that one ring nitrogen heteroatom be left free for *N*-glycoside bond formation. Pairing energies

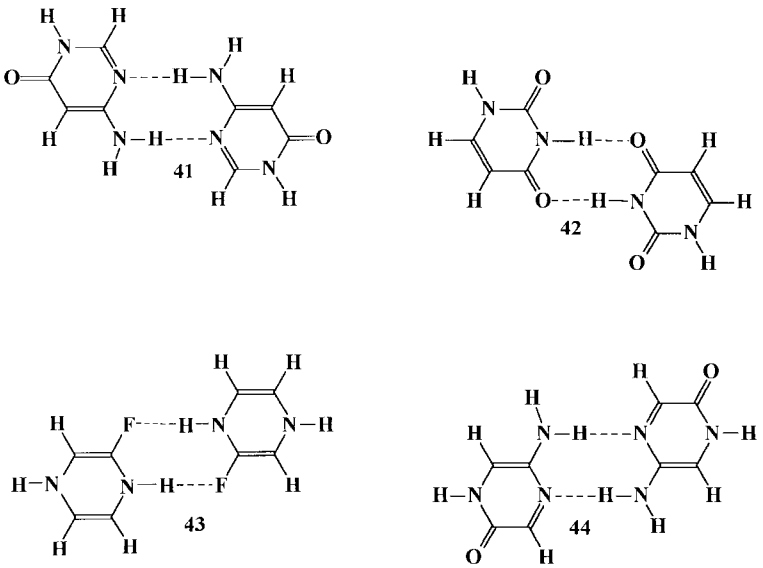

Fig. 5. Self-associative pairs for pyrimidine and pyrazine systems.

and hydrogen bond data for the two pyrimidine pairs **41** and **42** and the two pyrazine pairs **43** and **44** are given in Table 7, the pairs being portrayed in Fig. 5. While E_p values are all negative, the pair **42** with oxygen as the electronegative atom is more stable than those with fluorine (**41**, **43** and **44**). Since the hydrogen bonds are not quite linear, the E_p values here are not as large as expected.

The configurational data of Table 8 reveal that pairs **41** and **44** are more planar than the pairs **42** and **43**. The configurations are not quite the same, although the ϑ_1 and ϑ_2 markers have the range from 154.83 to 165.81°, which would thus allow for reversibility of each pair. These four bases were initially designed with the hope of arriving at a DNA-type quartet, but fall short of this aim since the pairs **43** and **44** departed from the initially assigned configuration during optimisation in order to allow for linearity of hydrogen-bonding.

4. Conclusions

The 34 pairs studied here indicate that only the imidazole pairs **21**, **28** and **35** allow for consideration together as DNA base mimics. Here the informational content would lie basically in the topology and steric arrangement of the pairs, from which a codon dictionary of 27 words may be built up. Hydrogen bonding is favoured by presence of oxygen rather than fluorine.

Acknowledgements

Thanks are due to the Computer Centre of this University for generous allocation of free computer time on the VAX 3100-40 system. D.M.L.B wishes to thank the University Grants Commission, Government of India, New Delhi, for financial assistance.

References

[1] J. Donohue, K.N. Trueblood, J. Mol. Biol. 2 (1960) 363.
[2] P. Hobza, C. Sandorfy, J. Am. Chem. Soc. 109 (1987) 1302.
[3] W. Saenger, Principles of Nucleic Acids Structure, Springer, New York, 1984, pp. 131.
[4] P. Hobza, Z. Havlas, Int. J. Quantum Chem. 36 (1989) 287.
[5] E. Uhlmann, A. Peyman, Chem. Rev. 90 (1990) 543.
[6] M.J. Lowe, M.J. Schellman, J. Mol. Biol. 65 (1972) 91.
[7] V.I. Poltev, I. Tinoco, J. Mol. Biol. 4 (1962) 500.
[8] D. Venkateswarlu, R.H.D. Lyngdoh, J. Chem. Soc. Perkin Trans. 2 (1995) 839.
[9] D. Venkateswarlu, M. Bansal, R.H.D. Lyngdoh, J. Chem. Soc. Perkin Trans. 2 (1997) 621.
[10] P. Hobza, J. Sponer, M. Polasek, J. Am. Chem. Soc. 117 (1995) 792.
[11] A.R. Leach, P.A. Kollman, J. Am. Chem. Soc. 114 (1992) 3675.
[12] J. Sponer, P. Hobza, J. Phys. Chem. 98 (1994) 3161.
[13] G. Robert, R. Maclagan, Aust. J. Chem. 32 (1979) 1635.
[14] I.R. Gould, P.A. Kollman, J. Am. Chem. Soc. 116 (1994) 2493.
[15] J. Florian, J. Leszezynski, J. Am. Chem. Soc. 118 (1996) 3010.
[16] J.J.P. Stewart, J. Comput. Chem. 10 (1989) 221.
[17] J. Donohue, Proc. Natl. Acad. Sci. USA 42 (1956) 60.
[18] R. Fletcher, M.J.D. Powell, Comput. J. 6 (1963) 163.
[19] W.C. Davidon, Comput. J. 10 (1968) 406.