Biophysical Chemistry 17 (1983) 75–86
Elsevier Biomedical Press

THE ELECTROSTATIC FIELD OF THE COMPONENT UNITS OF DNA AND ITS RELATIONSHIP TO HYDRATION

Richard LAVERY, Alberte PULLMAN and Bernard PULLMAN

Institut de Biologie Physico-Chimique, Laboratoire de Biochimie Théorique associé au C.N.R.S., 13, rue Pierre et Marie Curie, 75005 Paris, France

Received 13th July 1982
Revised manuscript received 20th September 1982
Accepted 6th October 1982

Key words: Electrostatic potential; Electrostatic field; DNA constituent; Hydration

The electrostatic fields of the subunits of DNA are presented and compared with the corresponding electrostatic potentials. Differences are observed between these two properties, due to their different dependence on distance, which are of considerable interest since, whereas the potential may be used in studying the reactivity of molecules towards charged species, the field can be a similar guide to attack by neutral, dipolar molecules such as water. It is demonstrated, for the example of the purine and pyrimidine bases, that the field may indeed be used to detect preferential hydration sites.

1. Introduction

The significance of the electrostatic properties of nucleic acids and their constituents as a guide to their reactive behavior has, in recent times, been clearly demonstrated [1,2]. Attention has been centered essentially in this respect on the molecular electrostatic potentials, which were studied in detail for various conformations of DNA (ref. 3 and references quoted therein) and for one transfer RNA, $tRNA^{Phe}$ [4,5]. These potentials led to many insights into the experimentally observed reactive properties of these biopolymers towards charged attacking species, most generally electrophiles. Recently, we have extended our studies to the computation of the associated molecular electrostatic fields [6–8], an extension which, besides its intrinsic interest, should be particularly useful for exploration of the interation of nucleic acids with neutral, dipolar species. Thus, whereas the potential enables us to ascertain the electrostatic energy of a point charge under the influence of a macromolecule, this energy being simply the product of the magnitude of the charge with the local potential, the field enables us to obtain the electrostatic energy of a point dipole, by calculating the scalar product between the moment of this dipole and the local field. Because of the polyanionic nature of nucleic acids, the electrostatic component of their interaction energy with an attacking species is generally dominating and often exerts a strong influence in favoring a particular reactive site. Thus, provided the attacking species is not too large or complex, the field should be a good guide to the behavior of neutral molecules of a dipolar nature, in the vicinity of the macromolecule. One species which falls into the latter category, and which is of no small biological importance, is the water molecule.

It should be noted that this use of fields implies a simple point-dipole model for water which might be thought, a priori, to be an oversimplification. We shall show by comparison with calculations involving accurate multicenter multipole expansions that rather satisfying correlations can nevertheless be obtained. This technique should thus be quite useful particularly as it can be applied, with relatively little expense, to macromolecular systems.

Work has begun to this end in our laboratory and several studies treating the distribution of the electrostatic field around B-DNA [6], A-DNA,

0301-4622/83/0000-0000/$03.00

Z-DNA [7] and tRNA$^{\mathrm{Phe}}$ [8] have been reported. These studies have clearly demonstrated that there are important differences between the distribution of the potentials and that of the fields of nucleic acids and that, in consequence, the confusion between these two measures, often encountered in discussions of electrostatic properties, must be avoided.

In order to interpret these differences for nucleic acids, it is useful to understand the differences which already exist at the level of the component parts of these macromolecules, namely the bases, phosphates and sugars. This is the aim of the present publication, in which the electrostatic fields surrounding each of these subunits are described and compared to the corresponding potentials, which have been previously presented in the literature [1,2,9–12]. It further gives us the opportunity to test the usefulness of electrostatic fields in predicting preferential hydration sites of the bases, by comparison with the sites determined in a series of earlier publications from this laboratory through calculations of the interaction energies [13,14]. We have chosen, in these studies, to limit ourselves to the conformations of the subunits corresponding to the most common allomorph of DNA, namely B-DNA, as given by Arnott and Hukins [15].

2. Method

The formulae used to calculate the potential, V, or field, $\boldsymbol{E}$, of a molecule are given below. Each contains two terms, the first due to the nuclei of charge Z_α at a distance of $r_{\alpha\mathrm{P}}$ from the point of calculation, P, and the second due to the electronic distribution $\rho(i)$ whose volume element $\mathrm{d}\tau_i$ is at a distance of $r_{i\mathrm{P}}$.

$$V(\mathrm{P}) = \sum_\alpha \frac{Z_\alpha}{|r_{\alpha\mathrm{P}}|} - \int \frac{\rho(i)\mathrm{d}\tau_i}{|r_{i\mathrm{P}}|}$$

$$\boldsymbol{E}(\mathrm{P}) = \sum_\alpha \frac{Z_\alpha \boldsymbol{r}_{\alpha\mathrm{P}}}{|r_{\alpha\mathrm{P}}|^3} - \int \frac{\rho(i)\boldsymbol{r}_{i\mathrm{P}}\mathrm{d}\tau_i}{|r_{i\mathrm{P}}|^3}$$

The field is simply the derivative of the potential with respect to distance, but this interrelation has two important consequences. Firstly, whereas the potential is a scalar quantity, the field is vectorial and, secondly, the field of a molecule will fall off much more rapidly with distance than its potential.

In order to obtain the nuclear contribution to the potential or field it is only necessary to know the nuclear coordinates, but to obtain the electronic contribution it is first necessary to calculate a molecular wave-function from which the corresponding electron density may be extracted. This requires quantum calculations and we have employed, in all our electrostatic studies, ab initio self-consistent field (SCF) wave functions of reasonable accuracy [16].

In calculating the electrostatic properties of nucleic acids it is clearly impossible to obtain a wave-function for the entire macromolecule. In order to overcome this difficulty, a technique was developed which consists of dividing the macromolecule into a number of subunits, small enough to be treated by the SCF formalism, and then superposing the properties, potential or field, of these subunits, appropriately oriented in space, to generate the macromolecular properties [1]. The subdivision of the macromolecule is made in such a way that the resulting electronic perturbations are minimized, which for nucleic acids implies divisions at the glycosidic bonds and at the backbone linkages $C_{3'}$–$O_{3'}$ and $C_{5'}$–$O_{5'}$. Saturation of the resulting free valencies with hydrogen atoms yields the subunits that we have used in all our studies of the nucleic acids, namely, the bases (in the case of the DNAs guanine, adenine, cytosine and thymine), an anionic phosphate, $H_2PO_4^-$ and a sugar, which, however, lacks its 3', and 5'-hydroxyl groups, since these groups are, by the nature of the subdivision, associated with the phosphate. It is these subunits that we shall study in the present publication, using the conformations corresponding to B-DNA due to Arnott and Hukins [15].

Since the calculation of electrostatic properties with the formulae given above is, nevertheless, rather time consuming, due to the integrals involved in the electronic term, it is advantageous to replace the continuous electronic distribution by a discrete multipole expansion. Such an expansion, termed OMTP or Overlap MulTiPole expansion, has been developed in our laboratory [17–19] and consists of a multipole center on every atom and at the midpoint of every atom pair, each center having a monopole, a dipole and a quadrupole (details of these expansions may be obtained from the authors upon request). This expansion allows accurate potentials or fields to be obtained down to 2 Å from any constituent atom of the molecule Under study [20]. Below this distance penetration effects invalidate the multipole representation and exact potentials or fields must be calculated. In the present publication we shall only discuss results beyond this boundary.

The electrostatic potentials and fields are calculated in planes, the values of these properties being indicated by various degrees of shading, darker zones corresponding to more negative potentials or stronger field intensities. Zones closer to the subunits than 2 Å, for which the electrostatic properties are not computed, are indicated by bounded blank regions. For each of the bases, two calculations are performed. Firstly, the potentials and fields are determined in the plane containing the base, the results henceforth being termed 'in plane', and secondly, the same properties are calculated in a plane parallel to the first, but distant from it by 2 Å, the results henceforth being termed 'parallel plane'. The latter calculations enable investigation of the electrostatic properties of the π-electron clouds of the bases. For the phosphate, only one plane containing the phosphorus atom and its two anionic oxygens is treated, and for the sugar, we also study a single plane, passing through its ring oxygen, $O_{1'}$, and perpendicularly bisecting the bond $C_{2'}-C_{3'}$. The latter two planes each contain the strongest calculated fields of the corresponding subunits.

Since the fields are vectorial quantities, we also indicate the field directions around the subunits with the aid of three symbols: a triangle (△) which indicates field vectors pointing out of plane and upwards by more than 30° from the plane studied, a distorted cross ( ) which indicates field vectors pointing out of plane and downwards by more than 30° and an arrow for vectors which are within 30° of the plane. Each of these symbols is, moreover, oriented to indicate the direction of the field component in the plane (in the case of the triangle and the distorted cross, this direction is from the broader end of the symbol to its narrower end).

The units that will be used for the fields are V/Å and, for ease of comparison, we give the potentials in V, rather than in the unit we have previously employed, namely, kcal/mol. The conversion to the latter unit demands only a multiplication by the factor 23.06.

The preferential hydration sites of the DNA bases that we will refer to are the results of monohydration studies performed by calculations of the electrostatic energies of interaction [13]. It has been verified [14] that these calculations are capable of reproducing very well the favored positions of hydration obtained with full quantum calculations in the ab initio SCF supermolecule approach.

3. Results and discussion

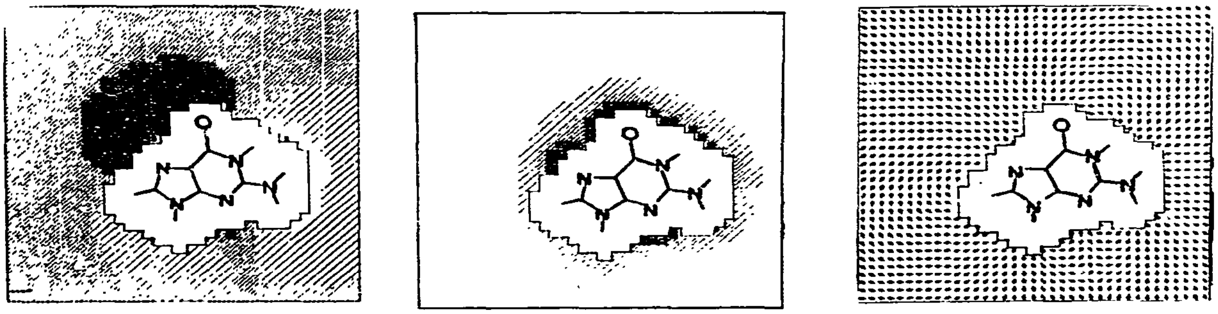
The electrostatic potentials and fields of the bases, guanine, adenine, cytosine and thymine, of the phosphate and of the sugar are presented in figs. 1–6. The details of the shadings used in these figures are given in Table 1, while the maximal and minimal potentials (indicated by the letters M and X in the figures) and the maximal field intensities

Table 1
Shadings used to represent potential, V (V) and field E (V/Å)

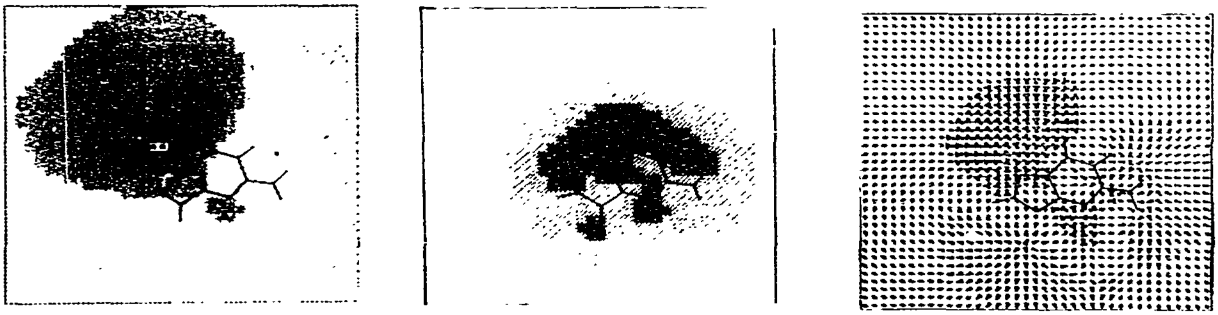
Shading	Bases (in plane)		Bases (in parallel plane)		Phosphate		Sugar	
	V	E	V	E	V	E	V	E
	1.39	0.0	0.91	0.0	−1.08	0.0	0.30	. . .
□	↓	↓	↓	↓	↓	↓	↓	↓
	0.78	0.27	0.52	0.15	−1.95	0.43	0.04	0.18
▨	↓	↓	↓	↓	↓	↓	↓	↓
	0.17	0.54	0.17	0.30	−2.82	0.87	−0.13	0.37
▨	↓	↓	↓	↓	↓	↓	↓	↓
	−0.43	0.81	−0.17	0.45	−3.69	1.30	−0.35	0.55
▩	↓	↓	↓	↓	↓	↓	↓	↓
	−1.04	1.08	−0.56	0.60	−4 55	1.73	−0.61	0.73
▦	↓	↓	↓	↓	↓	↓	↓	↓
	−1.65	1.35	−0.91	0.75	−5.42	2.17	−0.82	0.92
■	↓	↓	↓	↓	↓	↓	↓	↓
	−2.30	1.62	−1.34	0.90	−6.33	2.60	−1.08	1.10

Table 2
Maximal and minimal potentials and maximal fields in the planes studied

Unit	Potential minimum (V)	Potential maximum (V)	Field maximum (V/Å)
Bases (in the molecular plane)			
Guanine	−2.25	1.35	1.50
Adenine	−1.34	0.93	1.61
Cytosine	−1.99	0.93	1.42
Thymine	−1.23	1.18	1.33
Bases (parallel to the molecular plane)			
Guanine	−1.17	0.87	0.75
Adenine	−0.60	0.53	0.56
Cytosine	−1.26	0.57	0.87
Thymine	−0.64	0.69	0.64
Phosphate	−6.22	–	2.54
Sugar subunit	−1.07	0.26	1.07



In plane: (a) potential (b) field intensity (c) field direction



Parallel plane: (d) potential (e) field intensity (f) field direction

Fig. 1. Electrostatic properties of guanine. In the molecular plane: (a) potential, (b) field intensity, (c) field directions. In the parallel plane: (d) potential, (e) field intensity, (f) field directions.

are given in table 2. In each of the figs. 1–6 only the heteroatoms of the subunits are lettered, but the full standard atom notations may be found in fig. 7, which also summarizes the preferential hydration sites of each subunit (see refs. 13 and 14).

3.1. Guanine

The results for guanine are contained in fig. 1, the upper three diagrams giving the distribution of the potential (a), the distribution of the field intensity (b) and the field directions (c) around the base for the in plane calculations, and the lower three diagrams (d, e and f) giving the corresponding results for the parallel plane calculations (the same presentation is maintained for the other three bases studied).

The most negative potentials (the darkest zones) in the plane of guanine (fig. 1a) are seen to be associated with the electronegative atoms N7 and O6, somewhat weaker potentials being calculated close to N3. These two zones are separated by positive regions around the hydrogen atoms of the base. The field distribution (fig. 1b) also shows two more intense zones, but these are concentrated closer to the base than those of the potential. Further, the zone associated with atoms N7 and O6 is stronger close to atom N7, whereas the potential is more evenly distributed between the two atoms. This may be interpreted as the first illustration of the more rapid decline with distances of the field compared to the potential: the potentials due to N7 and O6 thus superpose to yield large magnitudes between these two atoms, even at a relatively appreciable distance from the base, whereas the shorter range field will be strong only close to the individual centers of high electron density. Note also that the closeness of these two centers of high electron density leads to the strongest potential (but not to the strongest field, see table 2) among all the bases studied. The field direction (fig. 1c) gives a relatively simple image: it always lies in the plane of the flat base, pointing towards regions of high electron density and away from regions of low density. The field thus points almost radially towards the centers N7, O6 and N3 but outwards from the base hydrogen atoms. These outward pointing fields turn back further away from the base to point towards the high electron density regions, thus making the overall field directions of guanine similar to those of a simple dipole.

The results in the parallel plane are somewhat different. The potential (fig. 1d) is now strong only over the atom pair N7, O6 and is most positive over the N2 amino nitrogen. The field intensity (fig. 1e) is rather concentrated over O6 and is somewhat weaker for the regions above N7 and N3. It is a general feature that, out of the molecular plane, the fields due to carbonyl oxygens are stronger than those due to the pyrollic ring nitrogens. The field directions (fig. 1f) still have a rather dipolar character, pointing up away from the hydrogens of the base and down towards the electronegative atoms. Table 2 shows that the magnitudes of both the negative and positive potentials and of the fields associated with the base are considerably weaker out of the molecular plane and this is also the case for the other bases studied.

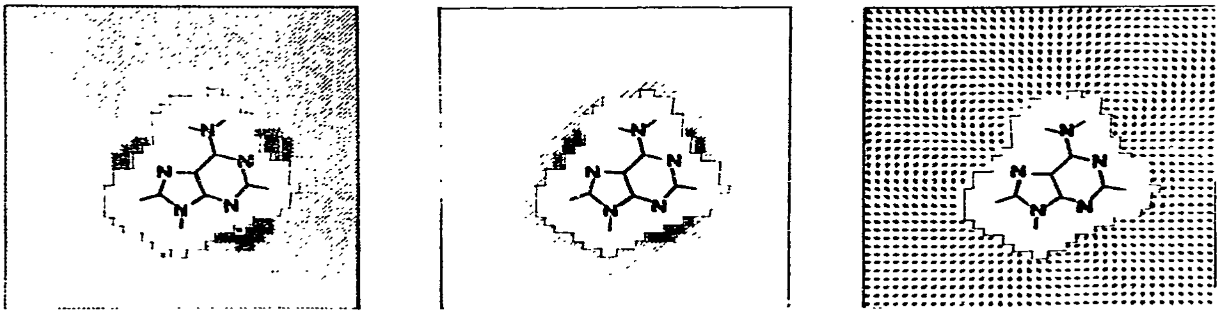
If we now compare the preferential hydration sites of guanine as obtained in ref. 13 (fig. 7a) with the preceding electrostatic properties it is seen that the distribution of the field is a very useful guide for determining these sites. Firstly, the fields surrounding guanine are much stronger in the plane containing the base than above and below it (see table 2, the same is true for the other three bases as well) and it is in this plane that the principal water-binding sites are found. Four strong water-binding positions have been located, the first bridging the atoms N7 and O6, the second and third on either side of N1-H and the fourth between N3 and N9-H. Each of these zones can be seen, in fig. 1b, to be associated with strong fields. In contrast, the potential is seen to be really strong only between N7 and O6 (where it is negative) and beyond N1-H (where it is positive). Strong water binding between O6 and N1-H or at N3 would thus not be easy to predict.

Moreover, the field allows the orientation of the bound water molecules to be easily understood. If the water molecule is replaced by a point-dipole model, this dipole, which is centered close to its oxygen atom and directed towards the midpoint between its two hydrogens, can clearly be seen to align with the local field (compare with fig. 1c) for each of the observed binding sites.

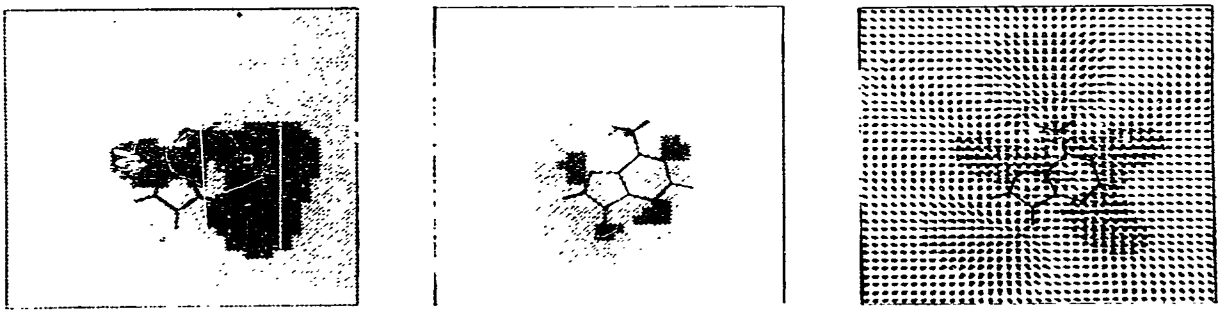
3.2. *Adenine*

The potential for adenine in the plane of the base (fig. 2a) shows three zones of negative values associated with the atoms N3, N7 and N1, the minimum occurring close to N3. The field (fig. 2b) also has three similarly located intense regions, but, as for guanine, these are more concentrated close to the base. Because of the existence of three zones of strong negative potential around adenine, rather than two as in the case of guanine, the field directions for adenine (fig. 2c) no longer have a simple dipolar character and it is thus understandable that the measured dipole moment of this purine (3.2 debye) is considerably weaker than that of guanine (6.9 debye) [21].

In the parallel plane of adenine (fig. 2d), there is one continuous zone of negative potential covering N7, N1 and N3, while the positive potentials occur principally over N9 and C8. The distribution of the field intensity (fig. 2e) once again shows the influence of the shorter range of the fields, the continuous zone seen for the potentials over N7, N1 and N3 being split up into three small isolated zones. There is also a fourth zone of strong field over the hydrogen of N9, for which the potentials were remarked to be relatively strong, but positive. The difference between this zone and the other three can be seen from the field directions (fig. 2f), which show upward pointing field vectors over N9-H, but downward pointing



In plane: (a) potential **(b) field intensity** **(c) field direction**



Parallel plane: (d) potential **(e) field intensity** **(f) field direction**

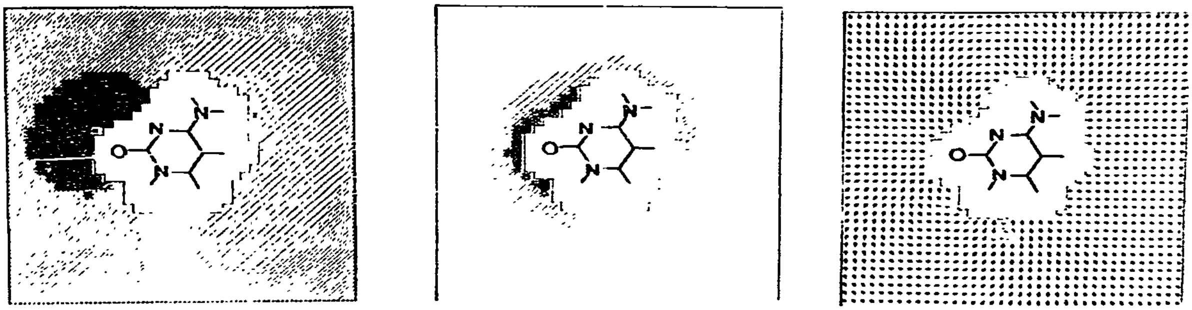
Fig. 2. Electrostatic properties of adenine. In the molecular plane: (a) potential, (b) field intensity, (c) field directions. In the parallel plane: (d) potential, (e) field intensity, (f) field directions.

ones over the three atoms with the high electron densities.

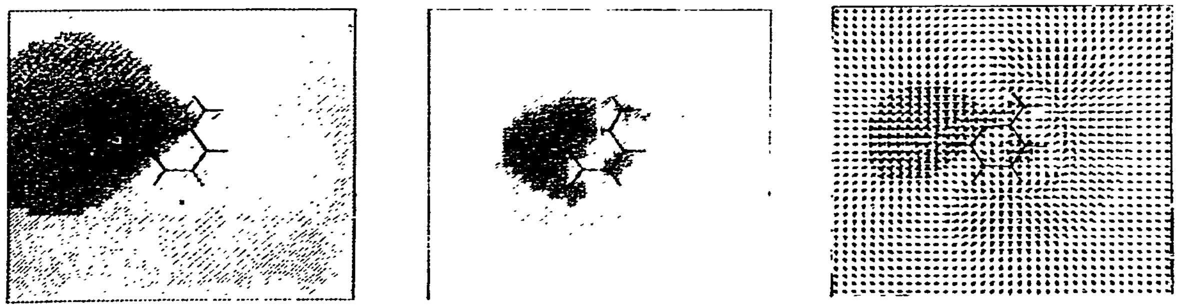
It is interesting to note that the strongest field intensity calculated in the molecular plane, for the four bases studied, is associated with adenine, whereas out of this plane this base manifests the weakest maximal field. This surprising reversal may be attributed to the alternation of regions of positive and negative potential around the periphery of adenine, which close to the base yields high potential gradients i.e., fields, but further away (for example, out of plane) rapidly cancel and give rise to only weak fields.

The preferential hydration sites of adenine are shown in fig. 7b. Three sites were found, between N7 and the amino group N6, between N1 and the amino group and between N9-H and N3. In each of these regions, closely related water configurations exist where the HOH plane is either parallel or perpendicular to the plane of the base. The correlation with the field distribution in fig. 2b is clear, three strong field zones being visible in the binding positions. By comparison with the field directions in fig. 2c, the bound water dipoles can be seen to be closely aligned with the local field. If water is again considered as a simple dipole (pointing from its oxygen atom to the midpoint of its two hydrogens), the existence of water-binding sites with similar energies, where the only change in configuration is a rotation of the water hydrogens out of the plane of the base, can easily be explained as such a rotation will not affect the alignment of the water dipole with the local field.

In the case of this base, the distribution of the potential (fig. 2a) also shows three zones of strong negative values close to the binding positions.



In plane: (a) potential (b) field intensity (c) field direction



Parallel plane: (d) potential (e) field intensity (f) field direction

Fig. 3. Electrostatic properties of cytosine. In the molecular plane: (a) potential, (b) field intensity, (c) field directions. In the parallel plane: (d) potential, (e) field intensity, (f) field directions.

However, that associated with N7 is weaker than the other two, whereas the water-binding energy is seen to be strong at this position (this is also the case for the field intensity). It should further be noted that the binding energy of water at N3 of adenine is the strongest of all the base sites and it is also at this position that the strongest of the base electrostatic fields is calculated. (The potentials are, in opposition, considerably stronger for the N7 site of guanine).

3.3. Cytosine

This base exhibits only one zone of strong negative potential in the molecular plane (fig. 3a), located between its carbonyl oxygen, O2, and its pyridine-like ring nitrogen, N3, the potentials surrounding the rest of the base being only weakly negative or positive. The field distribution (fig. 3b) is once again more concentrated around the base and, moreover, is split into separate zones around N3 and O2. The latter of these two zones extends considerably further around the carbonyl oxygen than the corresponding potential zone, which is partly due to the influence of the N1-H field contribution and also, probably, to a greater distinction between the two O2 lone-pair directions in terms of field than in terms of potential. The field directions (fig. 3c), like those of guanine, show a clear dipolar character, corresponding to a dipole pointing from O2 towards the bond C5–C6.

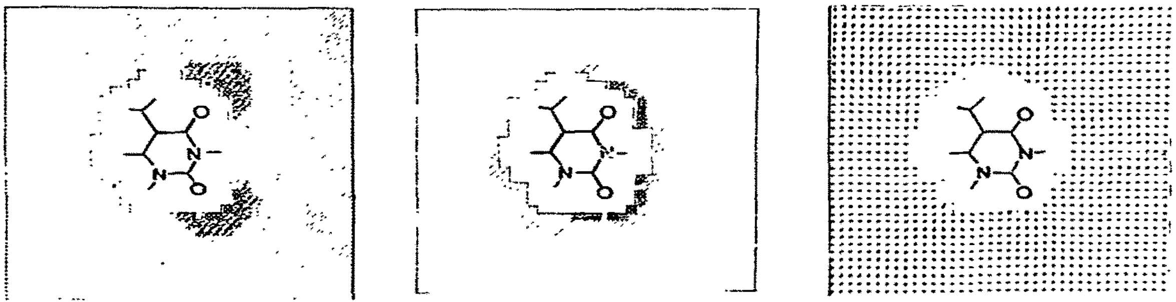
In the parallel plane of cytosine, the distribution of the potential (fig. 3c) is similar to that in the molecular plane, but the distribution of the field (fig. 3e) shows strong values over more extended zones covering O2 and N3, the maximum over O2 being the strongest of the values calculated in the parallel planes for the four bases studied. The field directions (fig. 3f) point upwards in a semicircular zone extending from the amino group to N1 and downwards over O2 and N3, as might be expected on the basis of the rather simple distribution of potential of this base.

Fig. 7c shows that there are two principal water-binding positions around cytosine, the first between O2 and N3 and the second between O2 and N1-H. The former site corresponds to the zone of the most negative potential (fig. 3a) and also to a zone of intense field (fig. 3b), but for the second site, only the field distribution has a corresponding maximum. Once again the orientations of the water molecule could be predicted very well from the electrostatic field vectors (fig. 3c).

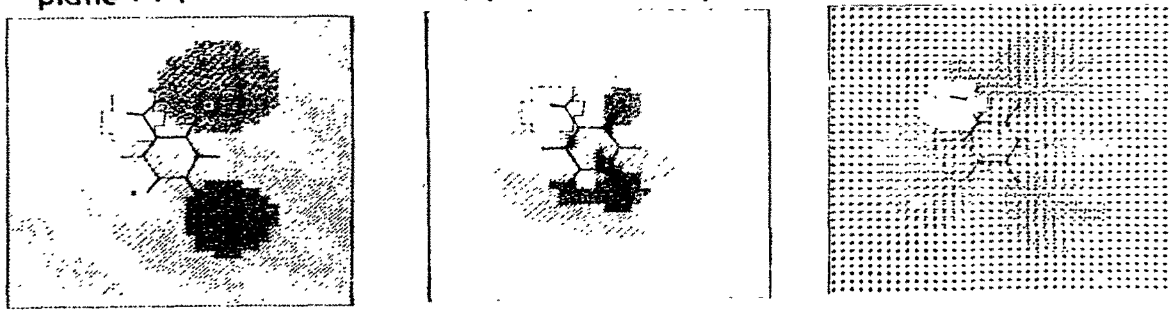
3.4. Thymine

The in-plane potentials of thymine (fig. 4a) show two strong negative zones over its carbonyl oxygens, O2 and O4, while on the opposite side of the base is an extended positive zone. As we may now expect, the field distribution (fig. 4b) resembles that of the potential with the exception that the fields are strongly concentrated around the base and the zones of intense field associated with the carbonyl oxygens are rather more extended around these atoms than the corresponding zones of potential, the short-range fields making a more important distinciton between the directions of the two lone pairs of electrons of each of these oxygens. The field directions (fig. 4c) point inwards to each of the carbonyl oxygens, whereas on the opposing side of thymine the fields point almost radially outwards.

The distribution of the potential in the parallel plane for this base (fig. 4d) is similar to that in the molecular plane and the minimum still lies close to O4. Thus, the protons of the C5 methyl group do not noticeably affect the potential of this carbonyl. In contrast, their effect on the field (fig. 4e) is clear, the strongest values of the field now being found over O2. This may again be explained by the shorter range of the field than of the potential. Above the base, one of the methyl protons is much closer to the plane than in O4. This situation influences the fields because the effect of O4 has considerably decreased, whereas it has little effect on the potential, the potential emanating from this center still being strong. The field directions (fig. 4f) are, as may be expected, towards the base over the electronegative atoms O2 and O4 and away from the base over the hydrogens bound to C5, C6 and N3. It is interesting to remark, in this connection, that both for cytosine and for thymine the electron density associated with the double bond C5–C6 is strong enough to turn the parallel plane fields towards the base in small regions over these atoms.



In plane: (a) potential (b) field intensity (c) field direction



Parallel plane: (d) potential (e) field intensity (f) field direction

Fig. 4. Electrostatic properties of thymine. In the molecular plane: (a) potential, (b) field intensity, (c) field directions. In the parallel plane: (d) potential, (e) field intensity, (f) field directions.

The principal water-binding positions around thymine are shown in fig. 7c in which three sites may be distinguished, one between O2 and N1-H and one on each side of N3-H. As for the preceding bases, the field distribution of thymine (fig. 4b) is a useful guide for finding these positions. The field is strong on both sides of oxygen O2 and on the side of O4 closest to N3, zones which correlate well with the locations of the molecules of water. In contrast, the strongest potentials, although they are also associated with the oxygens, are more centered along the directions of the carbonyl bonds.

3.5. Phosphate

In the plane of the anionic oxygens of the phosphate group we again observe the phenomenon of superposition of the potentials (fig. 5a), that is absent in the distribution of the corresponding fields (fig. 5b). For the potentials, the minimum occurs almost at the midpoint between these two oxygens, whereas the strong fields are separated into two zones. Not surprisingly, the net charge of the phosphate group leads to much stronger potentials and fields than those associated with the neutral subunits). The field directions of the phosphate (fig. 5c) present interestingly almost a simple radial distribution towards the molecule. This is an indication that from more than 4–5 Å away the phosphate will appear almost isotropic in this plane in terms of potential, which may be confirmed by looking again at fig. 5a, and this is also true in terms of field.

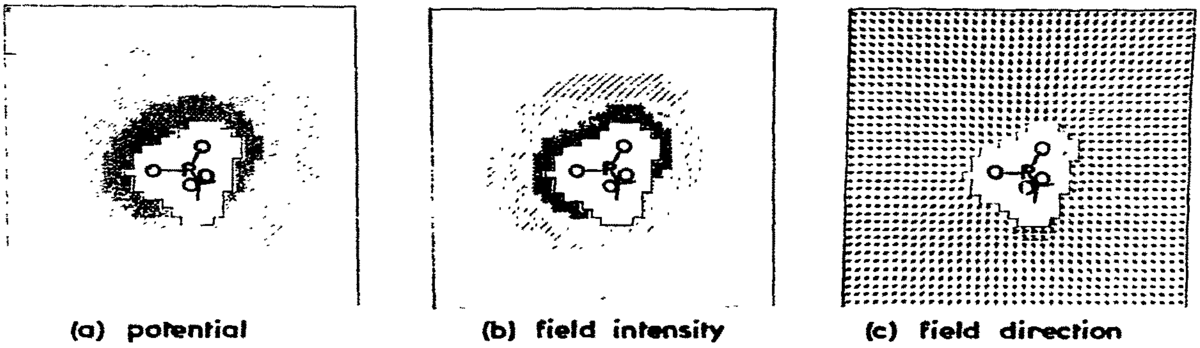

(a) potential (b) field intensity (c) field direction

Fig. 5. Electrostatic properties of the phosphate in the plane containing the phosphorus atom and the anionic oxygens. (a) Potential. (b) field intensity. (c) field directions.

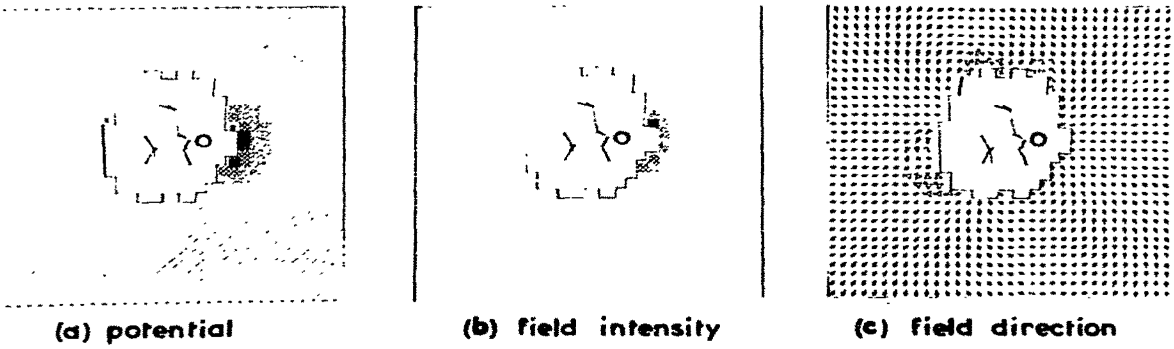

(a) potential (b) field intensity (c) field direction

Fig. 6. Electrostatic properties of the sugar subunit in the plane passing through its ring oxygen and bisecting perpendicularly the bond $C_{2'}$–$C_{3'}$. (a) Potential. (b) field intensity. (c) field directions.

3.6. *Sugar subunit*

Since the sugar subunit that we have studied lacks the deoxyribose hydroxyl groups at $C_{3'}$ and $C_{5'}$, there remains only one center associated with strong negative potentials (fig. 6a), namely close to the ring oxygen $O_{1'}$. The opposing side of the sugar subunit is uniquely associated with positive potentials, but it may be seen, as in the case of thymine, that this positive zone does not extend to encompass the hydrogens of the methyl group. The field of the sugar subunit (fig. 6b) is strong only around $O_{1'}$, the maximum occurring on the side of the $C_{5'}$ methyl. It may be noted from table 2 that the fields associated with this etheric oxygen are, however, somewhat weaker than those of the carbonyl oxygens of the bases. Fig. 6c shows that the field points outwards on the side of the $C_{2'}$–$C_{3'}$ bond and inwards towards the ring oxygen and also towards the $C_{5'}$ methyl, confirming the absence of repulsive potentials associated with this group.

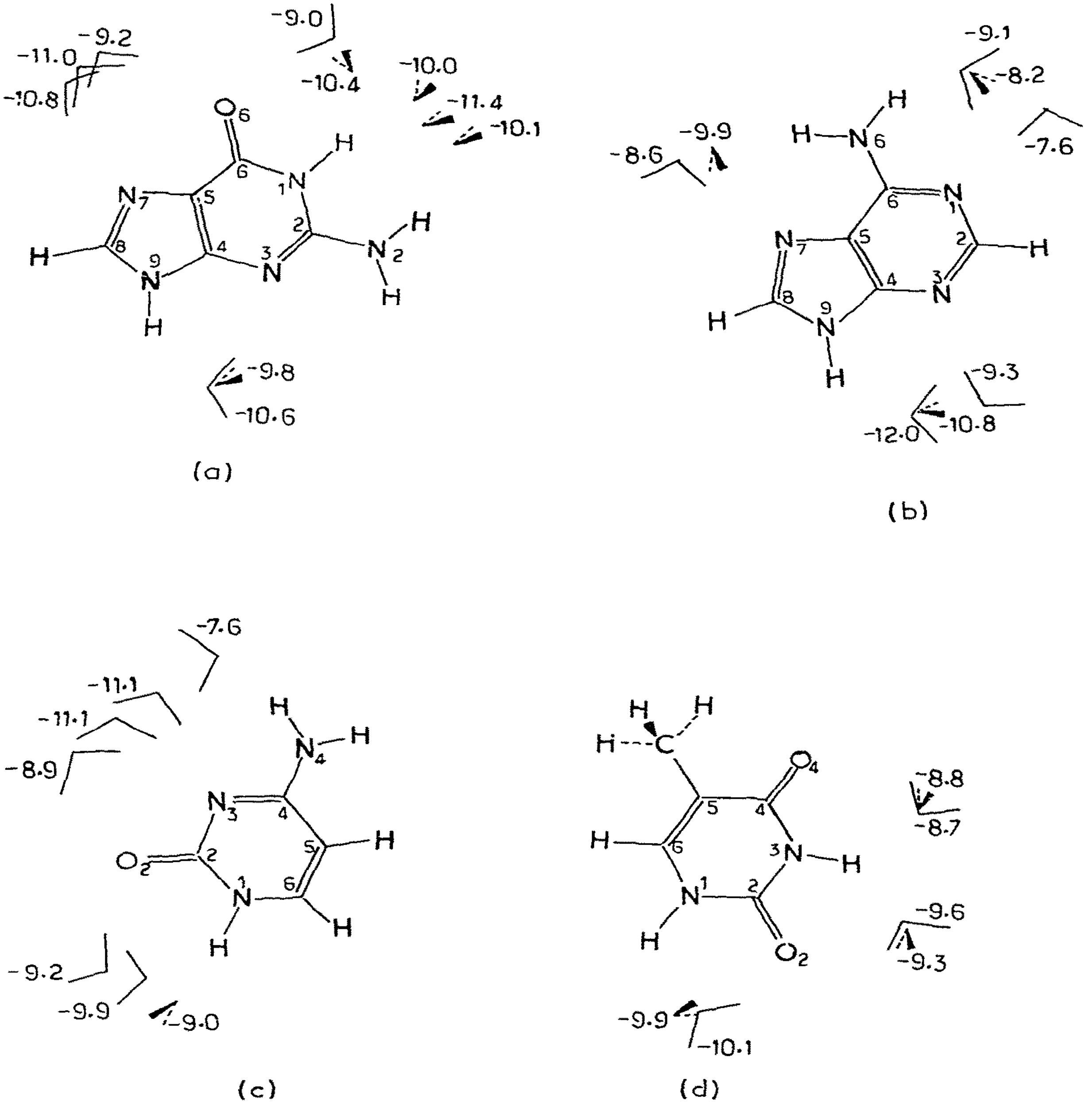


Fig. 7. The preferential water-binding sites of the DNA subunits (binding energies are indicated in kcal/mol, see refs. 13 and 14). (a) Guanine, (b) adenine, (c) cytosine, (d) thymine.

4. Conclusion

The comparison of the electrostatic potentials and fields of the subunits of B-DNA that we have carried out points to several important distinctions between these two properties. The differences are fundamentally linked to the more rapid decline with distance of the field compared to the potential. Close to the subunits, this leads to a clearer distinction of individual centers of high or low electron density in terms of field, since the superposition effects which occur with the potentials are considerably attenuated. In contrast, slightly further away from the subunits, whereas the potential distribution is generally rather similar, the field distribution can change radically, being much more sensitive to the distance of the various zones or high or low electron density in the molecule. In general, atoms of the subunits which are associated with either strong negative or strong positive potentials will also be associated with intense fields, but the ordering of these different sites in terms of potential and in terms of field is often different.

The distinctions between field and potential observed for the subunits of the DNA continue to exist, and are still more appreciable, once the macromolecule is constructed, as our studies of the conformations of B- [6], A- and Z-DNA [7] confirm. The situation may be simply summarized as follows: the nature of the distribution of potential around a molecule or a macromolecule is determined by an important superposition of potentials emanating from all its centers of high or low net charge density; for the field distribution these superposition effects are very much attenuated and these same centers largely retain their individual character. It is thus indeed important to distinguish between potential and field and, hence, between the electrostatic influence of a molecule or a macromolecule on a charged attacking species as opposed to a neutral dipolar species.

The correlations demonstrated between the field distributions in the subunits and water-binding sites and bound orientations obtained by accurate electrostatic interacton energy calculations suggest that fields are indeed a qualitatively useful guide to first-shell hydration.

References

1 A. Pullman and B. Pullman, Q. Rev. Biophys. 14 (1981) 289.
2 A. Pullman and B. Pullman, in Chemical applications of atomic and molecular potentials, eds. P. Politzer and D.G. Truhlar (Plenum Press, New York, 1981) p. 381.
3 B. Pullman, R. Lavery and A. Pullman, Eur. J. Biochem. 124 (1982) 229.
4 R. Lavery, A. Pullman, B. Pullman and M. de Oliveira, Nucleic Acids Res. 8 (1980) 5095.
5 R. Lavery, A. Pullman and S. Corbin, in Biomolecular sterodynamics ed. R.H. Sarma (Adenine Press, New Yor, 1981) p. 185.
6 R. Lavery, A. Pullman and B. Pullman, Theor. Chim. Acta, in the press.
7 R. Lavery and B. Pullman, Nucleic Acids Res. 10 (1982) 4383.
8 R. Lavery and A. Pullman, Proceeding of the 4th international congress of quantum chemistry, Uppsala, June 1982, in the press.
9 H. Berthod and A. Pullman, Chem. Phys. Lett. 32 (1975) 233.
10 H. Berthod and A. Pullman, Theor. Chim. Acta 47 (1978) 59.
11 H. Berthod and A. Pullman, CHem. Phys. Lett. 46 (1977) 249.
12 R. Lavery, M. de Oliveira and B. Pullman, J. Comp. Chem. 1 (1981) 301.
13 A. Pullman and B. Pullman, Q. Rev. Biophys. 7 (1975) 505.
14 A. Pullman and D. Perahia, Theor. Chim. Acta 48 (1978) 29.
15 S. Arnott and D.W.L. Hukins, Biochem. Biophys. Res. Commun. 47 (1972) 1504.
16 B. Pullman, N. Gresh, H. Berthod and A. Pullman, Theor. Chim. Acta 44 (1977) 151.
17 M. Dreyfus and A. Pullman, Theor. Chim. Acta 19 (1970) 20.
18 G.N.J. Port and A. Pullman, FEBS Lett. 31 (1970) 70.
19 A. Pullman and H. Berthod, Theor. Chim. Acta 48 (1978) 269.
20 A. Goldblum, D. Perahia and A. Pullman, Int. J. Quant. Chem. 15 (1979) 121.
21 B. Pullman and A. Pullman, Progr. Nucleic Acids Res. Mol. Biol. 9 (1969) 327.