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Aspects of the Electron Distribution in Adenine, Thymine and Cytosine as Given by Probability Density Curves from Nonempirical Calculations

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The electron probability density curves of adenine, thymine and cytosine are given and discussed.

Calculations of the nucleic bases, adenine, cytosine and thymine, have been carried out recently in our laboratory by a *non-empirical* self-consistent procedure in a Gaussian basis set. The essential results have been reported elsewhere [1] and discussed in a comparison [2] with those of empirical methods.

In order to gain more insight into the fine structure of the electron distribution in these large heterocycles we have used the wave functions obtained previously for drawing probability density contours maps, and we present here two of the most informative ones. Figs. 1a, b, c reproduce the contours for the total electron density in the molecular plane, and thus give the global aspect of σ bonding in these compounds. Fig. 2a, b, c, give the contours for the π-electron density in a plane parallel to the molecular plane at an altitude of 0.8 a.u. which corresponds approximately to the radial maximum of the nitrogen p atomic orbital in this direction, for the atomic set utilized.

As concerns the σ-contours, their most striking feature is probably *the constancy in the individual aspect of certain bonds, or atoms, or groups of atoms, in different environments:* one can observe, in particular, the characteristic shape of the carbonyl in thymine and cytosine, and the shape of the amino-group in adenine and cytosine. Such constancies are not limited to extra-cyclic substituents: inside the molecules, it can be seen that all the NH groups display a typical triangular form. Moreover all the pyridine-type nitrogens are characterized by another triangular distribution in which the directional character of the lone-pair is clearly visible. The carbon atoms appear globally very similar to one-another – even outside the cycles like in the methyl group of thymine. The carbon-carbon bonds of the cycles are well-characterized by a “ganglion-type” aspect. The CH bonds are more or less “fat” with an overall similarly: it may be worth noting here that the order of decreasing “fatness” of the CH bonds in cytosine and thymine follow the increasing order of the bond length adopted as input: 0.87, 1.00, 1.02 and 1.10 Å respectively. Moreover, the two CH bonds of adenine and the C_6H bond of thymine which come out very similar correspond to the same input length. This “fatness” of the CH bonds is also connected with the values of the corresponding overlap populations. The same correlation is observed for C–C bonds, but not for the bonds involving more electronegative atoms.

The fact that contours for NH_2, C–O, and CH very analogous to the present ones have been found in a recent study of formamide and its dimer by the same method [3], speaks in favor of the transferability of the global σ-characteristics of atoms or groups from one molecule to another and justifies the hypothesis of a localized σ-core in π-electron calculations, when no ionization or excitation is involved.

The localized character of the σ-cloud appears also in the relative symmetry of the hexacycle in adenine with respect to the C_2C_5 axis in spite of the substituent on C_6. A similar symmetry is seen in the cycle of thymine with respect to the same axis in spite of the carbonyl on C_4.

Another outstanding feature of the σ-diagrams concerns the "lone-pairs" in these molecules: as already mentioned, the pyridine-like nitrogens show a very distinct elongation of their electronic cloud towards the outside of the rings in

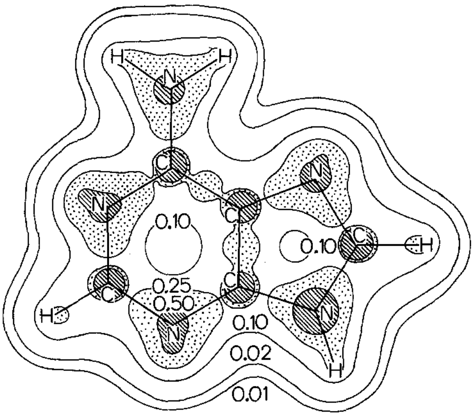

Fig. 1a

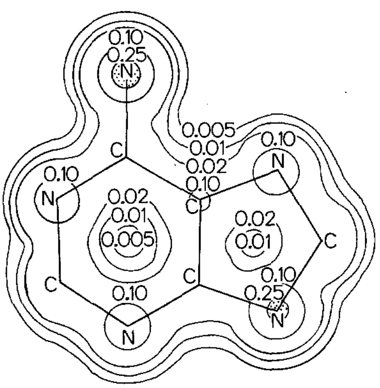

Fig. 2a

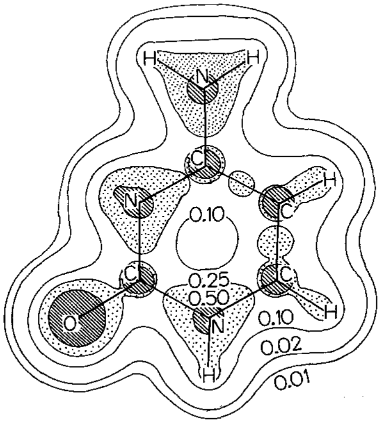

Fig. 1b

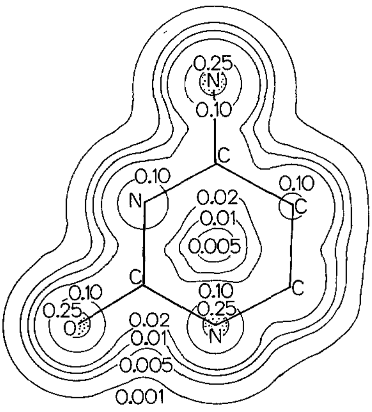

Fig. 2b

Fig. 1a–c. Contour of constant values of electron density in the molecular plane. Values as indicated. a Adenine; b Cytosine; c Thymine

Fig. 2. Same as in Fig. 1, but in a plane parallel to the molecular plane at 0.8 a.u. from it

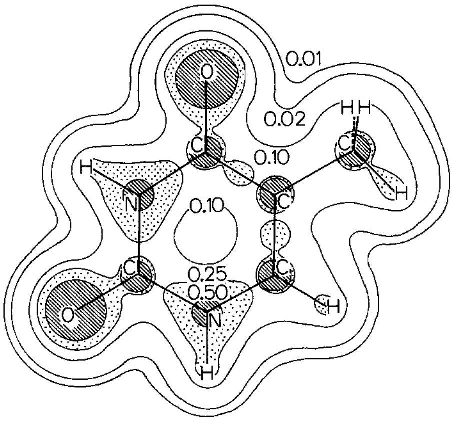

Fig. 1c

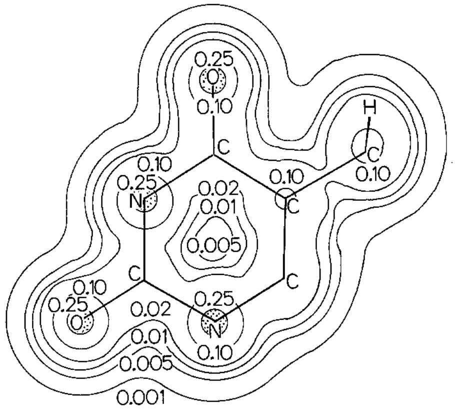

Fig. 2c

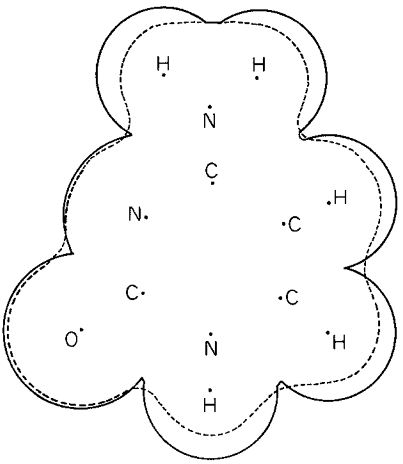

Fig. 3. Comparison of the 0.01 probability curve with the Van der Waals contour

a direction bissecting the external angle of the single bonds. On the contrary in the case of the carbonyl oxygens, no directional character appears in the electron distribution and the non-bonding electrons are entirely buried inside a practically spherical distribution. This last result is in agreement with the conclusions obtained by comparison of X-rays and neutron diffraction data on carbonyl oxygens [4]. It also agrees with the fact, recently stressed by Donohue [5], that the angles of the hydrogen bonds O... HX with the C=O direction for a carbonyl oxygen acting as proton-acceptor vary over a very wide range.

It is interesting to investigate how the external density contours obtained in such non-empirical computations compare with the notion of Van der Waals radii: Fig. 3 illustrates the comparison in the case of cytosine where the contour of 0.01 density in the molecular plane is reproduced together with the contour obtained in drawing cercles centered on each atom with the appropriate radius [6]. It is visible that the outside shape of the molecule is correctly given by the Van der Waals radii in the neighbourhood of the "heavy" atoms but that the possibilities of approach in the hydrogen regions are better than indicated by the mean radius. The two other molecules present the same situation.

As to the π-electron density, the map of adenine shows very neatly the distinction between the two types of nitrogens which must be defined in π-calculations: the "pyrrole-or amino-type" and the "pyridine-type" [7]. In the molecular field, the first ones loose part of their pair of π electrons while the second type gains π-charge over its original one-electron contribution. The final distribution shows more π-density left on the first kind than gained on the second. This agrees with the relative values found for the gross atomic populations [1]. Moreover, in the three molecules, π-electrons of NH_2 delocalize less than those of NH, in agreement with both the classical concepts and with the corresponding gross populations.

The carbon atoms of the cycles appear very little charged in π electrons with the exception of C_5 in the three molecules with a clearly larger extension of the high density region in cytosine. This result confirm thus the strong π-polarity of this particular atom, found in simple π-calculations [7] and later in various refined approximations [2, 8].

The carbonyl oxygens appear with a strong π-polarity.

A more detailed investigation of the density diagrams and of their utility will be given elsewhere as well as a study of the influence of the gaussian basis set utilized.

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