GRAPHICAL ESTIMATIVE OF DIAMAGNETIC ANISOTROPY IN SOME CONJUGATED SYSTEMS

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ABSTRACT

A graphical method for obtaining the diamagnetic anisotropy of certain conjugated systems relative to benzene's is proposed. The conjugation volume required is determined through the π charge density contour line of maximum conjugation. The agreement with experimental data or other theoretical treatments is satisfactory. In all the cases considered, not more than one third and not less than one fifth of each electron takes part in the conjugation.

INTRODUCTION

The quantum mechanical form of the current density operator associated with each j-th electron involves expressions of the type $\psi\nabla_j\psi$ [1]. The uncertainties in obtaining good wave functions, which are even greater for the gradients, explain the difficulty encountered when developing a rigorous theory of the diamagnetic anisotropies originated by the ring currents of conjugated systems. It is then no wonder that sometimes naïve methods, such as the free-electron Pauling model [2] may give better results than more sophisticated treatments [3] . It is clear than there is no satisfactory theory for the diamagnetic anisotropy in conjugated systems, and we do not aim to give it here. We shall restrict ourselves to sketch a semiempirical graphical scheme which may account for the diamagnetic anisotropy in this kind of systems as compared to benzene's ($\Delta K/\Delta K_B$).

It has been underlined, in concern with charge density distributions, that a "truly quantitative comparison of experimental and theoretical densities has not yet been achieved" [4]. In cyclic compounds one is particularly tempted to test this comparison through the characteristic diamagnetic anisotropy. It has been advanced [5] the hypothesis that the conjugation contour is related to the diamagnetic anisotropy, and we return now on this problem.

As we said, we obtain only relations and not absolute values. We are not able to calculate open-chain systems, yet we may account of certain "irregularities" as "tails" or lone pairs that enter into the conjugation. Of course, the whole of the anisotropy cannot be ascribed to the ring currents. But some

kind of scaling factor C may be assumed, such as in the case of the chemical shifts [6], so that our approximation is tantamount to setting $\Delta K = C\Delta K_{\pi}$.

THE CALCULATION

We shall follow a treatment quite similar to that shown by Salem [3]. The molecular contribution from ring currents J_r, to the diamagnetic anisotropy ΔK ($\Delta K = N_0 \chi_{\pi}$, N_0 Avogadro's number) is:

$$\chi_{\pi} = \frac{1}{c} \sum_r S_r (J_r/H) \qquad (1)$$

where the sum is over all irreducible circuits of the molecule, S_r is the area of the circuits, and H the applied magnetic field.

In Pauling's "free-electron" model [2], it is supposed that a π electron rotates about the direction of H with the Larmor frequency ω_L

$$-\omega_L = -eH/2mc \qquad (2)$$

and the current corresponding to this electron is

$$J = -e(+\omega_L/2\pi) = -e^2H/4\pi mc \qquad (3)$$

For the six π electrons in benzene, then,

$$J_{benz} = -3e^2H/2\pi mc \qquad (4)$$

Now, we shall suppose that <u>not the whole of the electron is free to move in the circuit, but only the part of it which</u>

conjugates. This is given by the maximum conjugation contour ρ [5], measured in $e/\mathring{A}^3$. To be consistent, instead of N = 6 electrons in benzene we shall have

$$Ne \Rightarrow \rho A h \tag{5}$$

where A is the conjugation area enclosed by ρ (see Fig. 1), which is measured graphically, and h denotes a mean height of the conjugation volume which may be supposed constant within the approximations involved (see discussion).

Figure 1

The relation between ΔK of any one cyclic molecule and benzene's would be then

$$\frac{\Delta K}{\Delta K_B} = \frac{\sum_r \rho_r^2 A_r S_r}{\rho_b^2 A_b S_b} \tag{6}$$

S is calculated supposing that each circuit in the molecule is a regular polygon whose side is the mean value of the interatomic distances.

We must add to expression (6) a semiempirical non-arbitrary factor f, which takes into account the existence of irregularities in the circuit, such as tails and lone pairs. Our final expression is

$$\frac{\Delta K}{\Delta K_B} = \frac{\sum_r \rho_r^2 A_r S_r f_r}{\rho_b^2 A_b S_b} \tag{7}$$

where the f_r factor is given by:

f_r = (number of vertex in the regular polygon to which the circuit is approximated)/(number of π electrons in the circuit) (8)

Since the conjugation contour enters squared in formula (7), we have taken care to determine it with three significant figures. The calculation of ρ is performed through the π part of the CNDO/2 fundamental state wave functions for each molecule. We thus ensure a self-consistency in the σ skeleton.

This semiempirical, almost wholly graphical estimate combines the simplicity of the Pauling model with the possibilities of more sophisticated treatments [7].

RESULTS AND DISCUSSION

Fig. 2 shows the molecules calculated. In hydrocarbons (except azulene and fluorene, that are taken from Sutton [8]), we suppose regular benzenic structures with interatomic distance 1.40 Å. The azine distances are those of ref. [9]; borazine's is 1.44 Å [10]. The biological molecules are taken from ref. [11].

Fig. 2

The simplification of the mean conjugation height h of (5) involved in (6) may seem striking. But we have drawn a number of conjugation diagrams along bonds, in planes perpendicular to the molecular plane, and all of them wholly justify our approximation (see Fig. 3). In a C-C bond, even between a binary and a tertiary carbon, h is 0.8 - 0.9 Å. Curiously enough, though the conjugation ρ values are appreciably different, h stays within these same limits for bonds between C and O or N atoms (Fig. 3-a) shows the case C-O). Borazine is an extreme case, the lowest ρ value of the three tables. From Fig. 3b), $h_N \sim 1.1$ Å and $h_B \sim 0.6$ Å, the mean value of both falling also within the assumed constant h.

Fig. 3

The experimental anisotropies are all referred to benzene's, whose value is taken to be -59.7×10^{-6} cgs emu [12].

Conjugation ρ values are all determined from diagrams drawn at 0.7 Å above the molecular plane [5], obtaining contour charge density lines such as those shown for benzene in Fig. 1. Every bond involved in two circuits implies an overlapping of conjugation areas A_r along it; the overlapping area appears thus twice, once for each circuit.

The factor f_r is 1 for practically all compounds of table I (also for every one of table II). There is generally a good agreement with the available experimental data. It has been remarked [13] that Pauling's theory does not distinguish between molecules as phenanthrene and anthracene where ΔK depends only on the rings' perimeter and area. In our approximation, as in London's, they differ. In anthracene and phenanthrene the contribution $(\Delta K/\Delta K_B)_1$ must be taken twice by the symmetry, $(\Delta K/\Delta K_B)_2$ being the contribution of the internal ring, which differs from that of the external ones.

Table I

It has been asserted [14] that both theory and experiment agree in ascribing to polybenzenic condensed hydrocarbons a higher anisotropy than that which would have a hypothetical compound of the same number of independent benzene rings. Salem's theoretical results [3] also follow this trend. Nevertheless, our results show an inverse behaviour, in agreement with more recent experimental data.

The experimental data for 1-and 2-naphthol [16] are probably considerably inaccurate, for by the same technique [19] $\Delta K/\Delta K_B$ for naphthalene was predicted to be 2.44, very different from more recent values [15]. In these less favourable cases, only some of the angular parameters defining the orientation of the molecule can be derived from magne-crystallic measurements [19],

leading thus to less reliable values. However, the result given for fluorene in the same source is probably more reliable. The authors group in the same series biphenyl, fluorene and phenanthrene, due to the striking similarity in the dimensions of their unit cells; in these favourable cases it is possible to determine the precise orientations of the molecule in the unit cell [19]. The result for biphenyl agrees with the other one reported in the table, within the errors of this kind of experimental methods. Moreover for phenanthrene $\Delta K/\Delta K_B$ is 2.78, in perfect agreement with the much more recent result we quoted.

Returning to 1- and 2-naphthol, we think that their anisotropy should be lower than naphthalene's, although in this case perhaps our factor exaggerates the tail-lone pair effect.

We have not found any experimental value for azulene. The pentagon is seen to give a contribution half that of the heptagon and, being ρ the same in both, this must be ascribed wholly to the bigger values of A_2 and S_2.

Trans-stilbene must be considered separately. As London [13], we are not able to deal with the open-chain case. Still, we may pick the conjugation curve which includes the chain atoms and divide it considering each one as a tail of the benzene ring such as 1- or 2-naphthol, with the corresponding f = 6/7. We can also simply take as a ρ value that of the benzene ring (which anyway gives results slightly different from the benzene ones). For the sake of illustration, the first alternative gives $\Delta K/\Delta K_B = 1.68$, a clearly unsatisfactory result. We have chosen the second one, which of course falls short of explaining the chain contribution, that must be added in a correct estimate, bringing $\Delta K/\Delta K_B$ closer to the experimental value.

Table II shows results for monocyclic azines and borazine. For pyridine, pyrimidine and s-triazine the agreement is quite satisfactory. For pyridazine and pyrazine the experimental data are in contradiction with what the authors themselves argue [21], i.e. that $|\Delta K|$ decreases on progressive replacement of the fragment -CH= by -N=, due to the decrease of the delocalization and consequently the π current. This is what we obtain, the trend being benzene > pyridine > diazines > s-triazine > s-tetrazine. We find somewhat surprising a prediction of $|\Delta K|$ in pyridazine and pyrazine higher than benzene's. The difficulties in handling substances as pyridazine are well known; also, these data are determined in solution and the solvent's influence is not wholly explained, particularly for pyrazine [21].

We have chosen to keep for benzene the widely accepted value of -59.7 (both for tables I and II), instead of that proposed in [21]. Recent measurements on benzene using the magnetic birefringence method in dilute solutions or gases display values which do not differ too much from the one we have adopted. Values obtained for dilute solutions are larger [21] than the adopted value whereas for gases they are lower [23]. Thus, as this technique is based upon experimental values such as the molecular polarisability anisotropy, of which there are seldom reliable values available [24], we keep the value given in [12].

As for borazine, we have quoted in the table Watanabe's [25] as experimental result, although it is subject to discussion. It is expected for borazine to have an appreciably lower $|\Delta K|$ than benzene's, due to the lower π current. The measured diamagnetic anisotropy of B-trichloroborazole is estimated to be [26] about 40 per cent of that of $C_6H_3Br_3$ or about 30 per cent of benzene's.

If, following the hypothesis advanced in ref. [26], the substitution would reduce the borazole anisotropy more than benzene's, our value of 51 per cent may be considered reasonable. The question, however, remains open.

Figure 4 shows the conjugation lines for adenine. It is seen that the tail cannot be left out of the conjugation area, and this is a quite general feature. Let us remark that ρ has different values for each circuit. Of course, the hexagon lowest ρ contour line continues in the pentagon and we cut it in order to draw the corresponding circuit. As for the pentagon, ρ closes in the upper part, but as it is seen, we cut it in the lowest left corner. The overlapping surface is taken into account for both values of A_1 and A_2.

Figure 4

When analyzing table III, the factor f_r in formula (7) becomes essential. It is introduced in order to decrease the anisotropy as must be the case when a charge gradient appears, reducing the ability of the π delocalized electrons to originate a Pauling-Pople current [27]. This happens in the presence of lone pairs; the tails taking part in the conjugation represent another irregularity which intuitively decreases the current. It is evident that the molecule which most resembles the Pauling model is benzene, being its circuit the nearest possible to an isolated circular one. The best correction factor we have found is Eq. (8), but of course there may be others equally satisfactory or better.

Table III shows our results for some biological molecules. For these compounds, there exists only an indirect estimate of the anisotropy, through experimental determination of their magnetic susceptibility [28]. For this reason we do not report the errors.

The difficulties exhibited by the molecules containing the CO group have been already underlined [29], and some theoretical values are very low [30]. It has been suggested that the atomic contributions are the predominant factor instead of the π currents [29]. In our case, always referring to the CO group, the values are generally somewhat higher than those given in [28], differing from them in about 24% for guanine and xanthine. It is possible that by involving the tails, our conjugation areas give an excessive contribution (for example, A_1 in guanine is 87% bigger than benzene's). Of the CO-containing compounds, uric acid is the only one with a lower anisotropy than that of ref. [28].

Considered separately from each other (relative to [28]), our results compare favourably with those of [29], which were obtained following a Pople-type [31] method for magnetic susceptibilities in organic molecules.

The hexagonal cycles show the maximum ($\Delta K/\Delta K_B$) value in purine, decreasing first for adenine due to the NH_2 group and then in the CO-containing compounds, both in purinic and pyrimidinic bases. This was also pointed out in [32]. By the definition of our f_r the decrease effect is additive starting from purine, with one single π lone pair, up to uric acid, with the highest number of "irregularities" (two CO tails and two π lone pairs in the nitrogens). On passing from hypoxanthine to guanine the diminution effect of the NH_2 tail is also observed.

Of course, if the trend would actually be that predicted by our f_r, uric acid, being subjected to the highest number of irregularities, should have the lowest diamagnetic anisotropy. This is not the case with the reported indirect estimate.

The conjugation lines are systematically higher in the pentagon rings than in the hexagons.

It is not easy to distinguish the separate effects of the NH_2 and CO groups, and the π lone pairs, because they may overlap in the same molecule. An argument in favour of our assumption that a π lone pair lowers the diamagnetic anisotropy of aromatic molecules may be the consideration of a hypothetical limiting case of a benzenoid N_6H_6 molecule. According to the complementarity condition [33], it would have π electronic charges of 2, all zero π bond orders and therefore no delocalization and no diamagnetic anisotropy due to the π current. A complementary state of one which affords a certain diamagnetic anisotropy due to its π current, must then have a π paramagnetic anisotropy of the same absolute value, and viceversa.

Finally, from the three tables it may be drawn the conclusion that <u>not more than one third and not less than one fifth of each electron takes part in the conjugation</u> and consequently in the ring currents of the cyclic compounds considered in this paper.

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FIGURE CAPTIONS

Fig. 1 - Charge density contour lines (in $e/\mathring{A}^3$) in benzene, in a plane parallel to the molecular plane at a distance of 0.7 $\mathring{A}$ from it. $\rho = 0.337\ e/\mathring{A}^3$.

Fig. 2 - The molecules calculated in the present paper. The labellings correspond to those of tables I, II and III.

Fig. 3 - Conjugation diagrams along bonds, in planes perpendicular to the molecular plane: a) C-O bond in cytosine; b) B-N bond in borazine.

Fig. 4 - Conjugation diagrams of adenine, in a plane parallel to the molecular plane at a distance of 0.7 $\mathring{A}$ from it. The circuits of the hexagon and the pentagon are shown separately.

TABLE I

AROMATIC HYDROCARBONS. $\gamma = \Delta K/\Delta K_B$. A AND S ARE GIVEN IN $\mathring{A}^2$

Molecule	ρ_1	A_1	S_1	f_1	γ_1	ρ_2	A_2	S_2	f_2	γ_2	γ_{tot}	γ_{exp}	error (%)
(1) Benzene	0.337	4.80	5.09	1	1						1	1	
(2) Naphthalene	0.310	5.66	5.09	1	0.998						1.996	1.93 [15]	3
(3) Anthracene	0.270	6.60	5.09	1	0.883	0.292	6.32	5.09	1	0.988	2.754	2.88 [15]	4
(4) Phenanthrene	0.314	5.55	5.09	1	1.004	0.273	7.04	5.09	1	0.962	2.970	2.78 [15]	7
(5) Pyrene	0.315	5.06	5.09	1	0.921	0.256	7.74	5.09	1	0.930	3.702	3.90 [15]	5
(6) Azulene	0.245	6.50	4.03	1	0.567	0.245	8.36	6.26	1	1.132	1.699		
(7) Fluorene	0.229	7.01	5.10	1	0.675	0.229	6.08	4.24	1	0.487	1.837	2.03 [16]	9
(8) Biphenyl	0.319	5.42	5.09	1	1.012						2.024	1.99 [17] 1.81 [16]	2 12
(9) Trans-stilbene	0.331	5.12	5.09	1	1.029						2.058	2.37 [18]	13
(10) 1-Naphthol	0.314	5.67	5.09	1	1.025	0.235	9.07	5.09	6/8	0.689	1.714	2.40 [16]	28
(11) 2-Naphthol	0.316	5.69	5.09	1	1.042	0.236	8.86	5.09	6/8	0.679	1.721	2.44 [16]	29

TABLE II

MONOCYCLIC AZINES AND BORAZINE. $\gamma = \Delta K/\Delta K_B$. A AND S ARE GIVEN IN $\mathring{A}^2$

Molecule	ρ	A	S	f	γ	γ_{exp}	error(%)
(12) Pyridine	0.310	5.38	4.97	1	0.926	0.96 [20]	4
(13) Pyridazine	0.274	6.08	4.92	1	0.809	1.12 [21]	28
(14) Pyrimidine	0.310	5.00	4.92	1	0.852	0.84 [21]	1
(15) Pyrazine	0.309	5.32	4.79	1	0.877	1.17 [21]	25
(16) S-triazine	0.310	4.76	4.88	1	0.804	0.82 [22]	2
(17) S-tetrazine	0.270	5.60	4.83	1	0.711		
(18) Borazine	0.205	6.26	5.39	1	0.511	0.61 [23]	15

TABLE III

SOME BIOLOGICAL MOLECULES. $\gamma = \Delta K/\Delta K_B$. THE VALUES BETWEEN PARENTHESIS IN THE COLUMN γ_{tot} ARE THOSE OF REF. [29]. A AND S ARE GIVEN IN A^{02}

Molecule	ρ_1	A_1	S_1	f_1	γ_1	ρ_2	A_2	S_2	f_2	γ_2	γ_{tot}	γ[28]
(19) Imidazole	0.362	4.10	3.61	5/6	0.582						0.582(0.53)	0.627
(20) Cytosine	0.282	8.12	4.80	6/10	0.670						0.670(0.57)	0.655
(21) Uracil	0.273	8.19	4.90	6/10	0.647						0.647(0.49)	0.627
(22) Purine	0.300	5.83	4.71	1	0.891	0.314	4.82	3.61	5/6	0.515	1.406(1.38)	1.43
(23) Adenine	0.290	7.26	4.71	6/8	0.777	0.334	4.58	3.61	5/6	0.554	1.331(1.33)	1.29
(24) Guanine	0.275	8.98	4.79	6/10	0.703	0.348	4.47	3.67	5/6	0.597	1.300(1.0)	1.05
(25) Xanthine	0.270	8.80	4.79	6/10	0.664	0.351	4.30	3.67	5/6	0.584	1.248(0.95)	1.01
(26) Hypoxanthine	0.276	7.69	4.79	6/8	0.758	0.347	4.38	3.67	5/6	0.581	1.339(0.99)	1.19
(27) Uric acid	0.284	7.61	4.79	6/10	0.636	0.318	5.76	3.67	5/8	0.481	1.117(0.77)	1.23

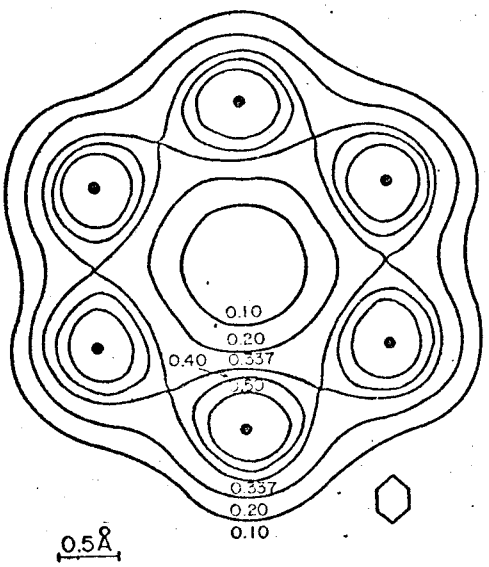

Fig. 1

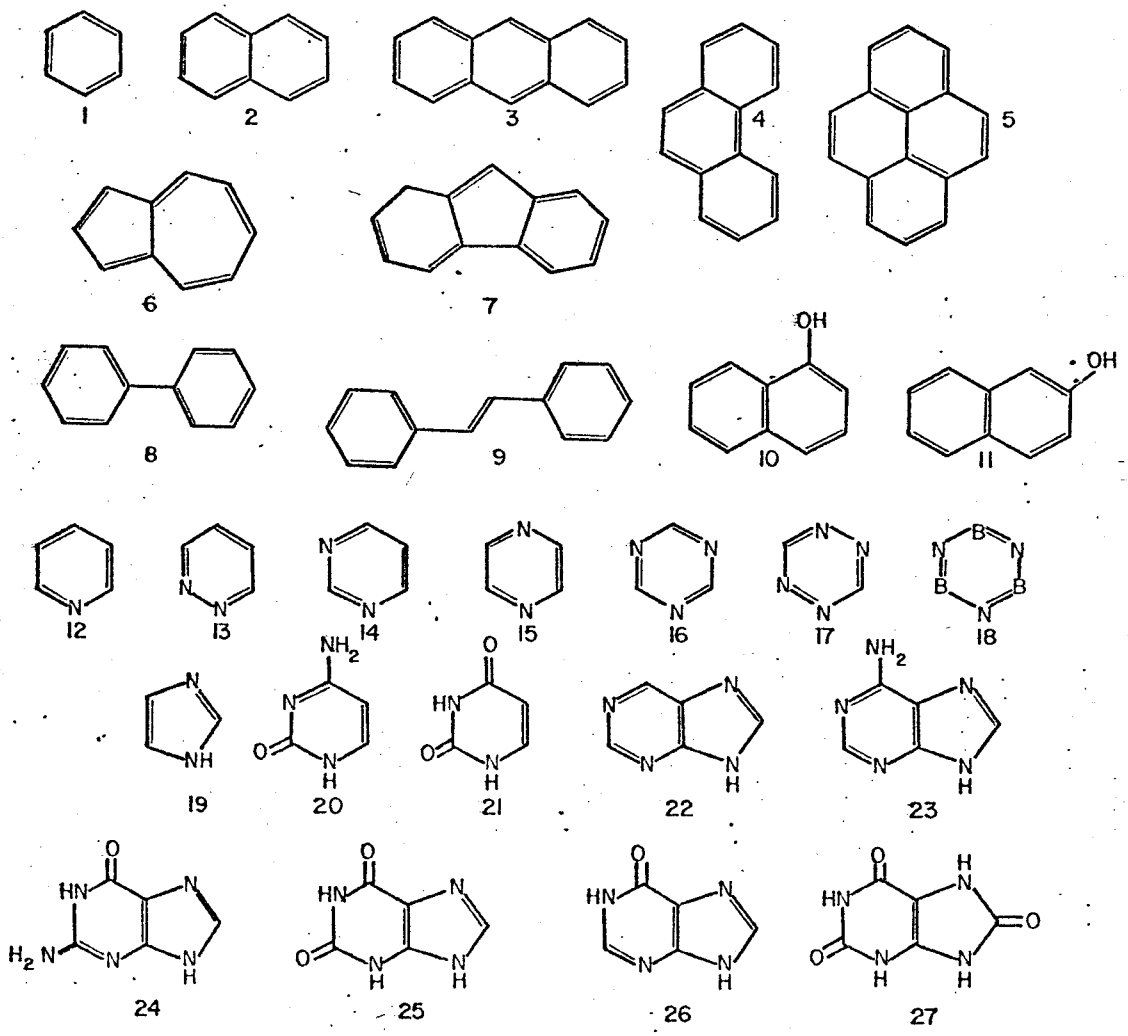
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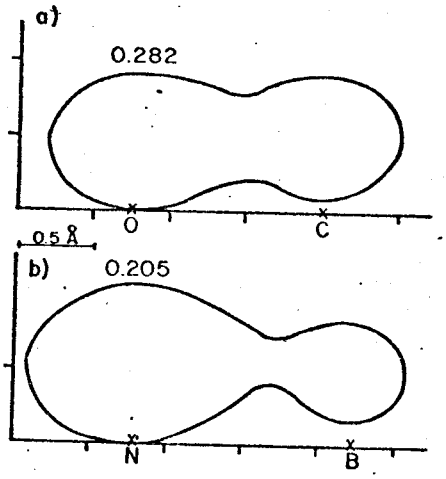
Fig. 2



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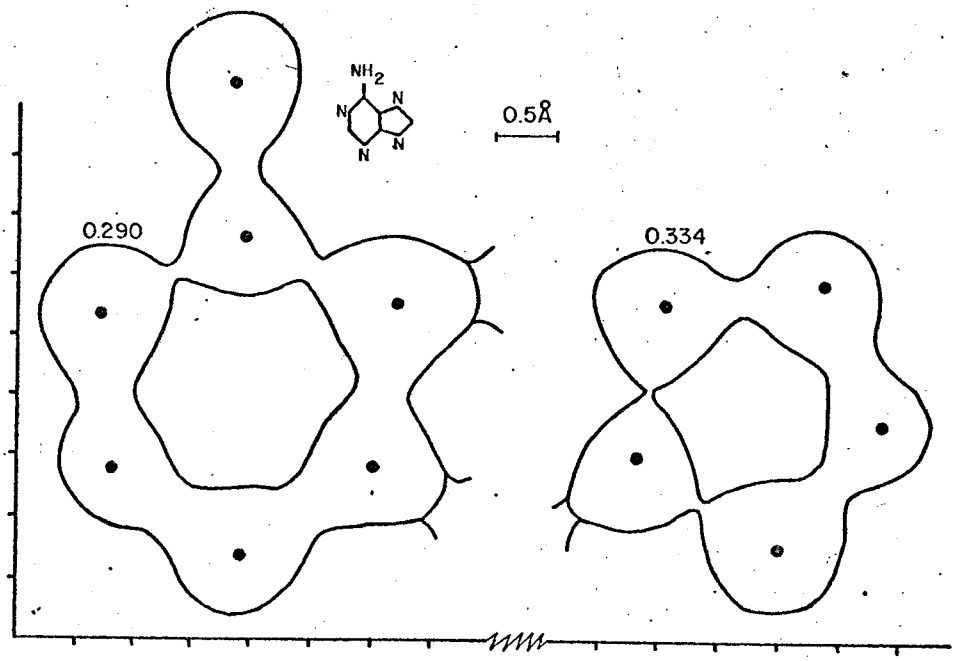

Fig. 4