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Modified Iterative Extended Hückel: II. Application to the

Interaction of Na^+, Na^+(aq.), Mg^{+2}, Mg^{+2}(aq.) with Adenine and Thymine

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ABSTRACT

Modified Iterative Extended Hückel, which includes explicit effective
internuclear and electronic interactions, is applied to the study of the
energetics of Na^+, Mg^{+2}, Na^+(aqueous), and Mg^{+2}(aqueous) ions approach-
ing various possible binding sites on adenine and thymine. Results for
the adenine + ion and thymine + ion are in good qualitative agreement
with a limited basis set _ab initio_ work on analogous systems (adenine
and uracil); energy differences between competing sites are in excellent
agreement. Hydration appears to be a critical factor in determining
favorable binding sites. The result that the adenine N1 and N3 sites
cannot displace a water molecule from the hydrated cation ($Ion \cdot 4H_2O$)
indicates that they are not favorable binding sites in aqueous media.
Of those sites investigated, O4 was the most favorable binding site on
the thymine for the bare Na^+ (a full determination was not made with
Mg^{+2}). However, the O2 site was the most favorable binding site for
either hydrated cation. Adenine and thymine results are consistent with
experimental findings [Mg^{+2}(aqueous)].

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Key words: Hückel, Binding sites, Hydrated cation interaction

1. Introduction

An ab initio investigation of the interaction between cations and mole-
cules of biological interest has been pursued in a series of recent
articles [1,2,3,4]. The motivation, in part, arises from the fact that
standard semiempirical methods either fail completely or are inadequate
when applied to systems which are sensitive to charge transfer. For
example, the failure of CNDO to correctly predict the most likely bind-
ing site of a cation on the uracil molecule [2] is due to its inability
to deal properly with charge transfer. Similarly, Iterative Extended
Hückel (hereafter, IEH) overestimates charge transfer and exhibits prob-
lems in achieving self-consistent charge distributions. These failings
are discussed in paper I [5] of this series. Modifications to IEH,
which include explicit effective internuclear and electronic interaction
terms, are detailed in paper I. These modifications should compensate
for some of the inherent deficiencies of IEH, such as the problems
associated with charge transfer. Therefore, the application of the
modified IEH program to cation-biomolecular systems is a critical test
of the usefulness of the modifications to IEH. Adenine and thymine were
chosen for study as substrates for ion-binding because they are rela-
tively simple; moreover, calculations have been carried out either with
these or similar structures [2,4]. The adenine and thymine struc-
tures [6], along with the possible binding sites that were considered,
are depicted in Figs. 1 and 2. The possible binding sites were limited
to those considered in Refs. [2,4]. Thus, N9 on adenine, or N1, N3 on
thymine were not examined. The workers in Refs. [2,4] did not attempt
a global search; consequently, since our interest was to make as direct

a comparison as was feasible, we also restricted our probing of the potential surface to cuts within the plane of the adenine and thymine molecules. The bare Na^+ and Mg^{+2} cations were used to probe those sites noted in Figs. 1 and 2. After determining the most favorable sites for the bare ions, hydrated forms were then introduced and the most favorable sites redetermined. This more complete modelling of cation-biomolecule binding has not been attempted previously, to our knowledge. The modified IEH program has been described in detail in paper I; however, a brief description will be offered in the following section.

2. Modified Iterative Extended Hückel

The program builds upon and extends conventional IEH. Explicit effective nuclear interaction terms are included. Let Z_i(valence) be the resultant nuclear charge after assuming that the core electrons completely shield their respective number of positive charges. Between the ith and jth atoms, which are separated a distance R, we set

$$(Z_i Z_j)_{effective}^{(\ell)} = \left[Z_i(valence) - \sum_{k(i)} P_{k(i)}(0,\tfrac{1}{2}R) \rho_{k(i)}^{(\ell)} \right]$$
$$\cdot \left[Z_j(valence) - \sum_{m(j)} P_{m(j)}(0,\tfrac{1}{2}R) \rho_{m(j)}^{(\ell)} \right]. \qquad (2.1)$$

Here, $P_{k(i)}(0,\tfrac{1}{2}R)$ is the probability of finding an electron in the kth orbital located on the ith atom in a spherical volume of radius $\tfrac{1}{2}R$. Similarly defined is $P_{m(j)}(0,\tfrac{1}{2}R)$. The term $\rho_{k(i)}^{(\ell)}$ is the electronic density assigned to the kth orbital after the ℓth iteration. The term $\rho_{m(j)}^{(\ell)}$ has a similar significance with regard to the mth orbital on the jth atom. The effective product

$$(Z_i Z_j)^{(\ell)}_{\text{effective}} \rightarrow Z_i(\text{valence}) Z_j(\text{valence}), \quad R \rightarrow 0; \qquad (2.2a)$$

on the other hand,

$$(Z_i Z_j)^{(\ell)}_{\text{effective}} \rightarrow q_{i,\ell} q_{j,\ell}, \quad R \rightarrow \infty, \qquad (2.2b)$$

where $q_{i,\ell}, q_{j,\ell}$ are the net charges on the $\underline{i}$th and $\underline{j}$th atomic centers. The contribution to the total energy made by the effective nuclear-nuclear interactions after the $\underline{\ell}$th iteration is given by

$$E^{(\ell)}_{\text{effective nuc-nuc}} = \sum_{i \neq j} (Z_i Z_j)^{(\ell)}_{\text{effective}} / R_{ij} \qquad (2.3)$$

in atomic units. In a similar vein, the molecular environment is sensed more directly by introducing coulombic modifications to the valence orbital ionization energies. Here, an electron in the $\underline{k}$th orbital on the $\underline{i}$th atom (which also is taken to be the $\underline{i}$th atomic type, for convenience) interacts with the electronic densities assigned to the orbitals on the $\underline{j}$ centers. A set of variables, which depends only on atomic types, is formed, and the variables are determined either by requiring specific charges (as was done in paper I) or are determined by variational considerations. This increment to the valence orbital ionization energy is expressed as

$$h_{k(i)} \equiv \sum_j \delta\varepsilon_{k(i),j} = \sum_j a_{ij} \cdot \Sigma\rho^{(\ell)}_{s(j)} \int \phi^2_{k(i)} r^{-1}_{k(i),s(j)} \phi^2_{s(j)} d\tau . \qquad (2.4)$$

The (a_{ij}) are the set of variables depending only on atomic type; $\rho^{(\ell)}_{s(j)}$ is the electronic density assigned to the $\underline{s}$ orbital on the $\underline{j}$th atom after the $\underline{\ell}$th iteration. The coulombic integral involves the two

atomic centers, $\underline{i}$ and $\underline{j}$, through their respective orbitals, $\phi_{k(i)}$ and $\phi_{s(j)}$. The initial diagonal elements of the Hamiltonian matrix are now given by

$$H_{k(i),k(i)} = H_{k(i),k(i)}^{(0)} + h_{k(i)} . \qquad (2.5a)$$

The off-diagonal elements

$$H_{k(i),s(j)} = \tfrac{1}{2}KS_{k(i),s(j)}\left[H_{k(i),k(i)} + H_{s(j),s(j)}\right] . \qquad (2.5b)$$

The symbol K is an interaction constant set equal to 1.89; $S_{k(i),s(j)}$ is the integrated overlap between orbitals $\underline{k}$ on the $\underline{i}$th atom, and $\underline{s}$ on the $\underline{j}$ atom. The eigenvalues of the Hamiltonian matrix may now contain two-electron contributions, but these are included in a fashion which permits the energies to be treated as though they were one-electron energies. The total molecular energy after the $\underline{\ell}$th iteration for a system composed of $\underline{m}$ atoms and N orbitals is given by

$$E_{total}^{(\ell)} = \sum_{u=1}^{N}\eta_u\varepsilon_u^{(\ell)} + \sum_{i\neq j}^{m}(Z_iZ_j)_{effective}^{(\ell)}/R_{ij} \qquad (2.6)$$

where η_u is the occupational number and $\varepsilon_u^{(\ell)}$ is the energy of the $\underline{u}$th molecular orbital. The first term on the right-hand side of Eq. (2.6) obeys a variational principle, from paper I. The E_{total} does not, in general, since some of the $(Z_iZ_j)_{effective}$ terms may grow more positive with successive iterations, before charge self-consistency is achieved. Standard IEH parameters were used in the calculations, and these are collected in Table 1. No attempt was made to optimize these

parameters for the systems considered. Within the framework of the Modified IEH, however, the energy values do represent optimum values given the constraints of stability (oscillation) and minimum electronic energies. The coefficients a_{ij} in Eq. (2.4) were determined to ±0.005. All calculations were performed on the NASA-Ames CDC 7600.

3. Results

3.1 Adenine

Adenine + ion results for both Na^+ and Mg^{+2} are displayed in Fig. 3. These ions were restricted to pathways in the plane of the molecule which bisected the bond angle of a site. Energy values are relative to the isolated adenine, i.e., $\Delta E = E_{(adenine + ion)} - E_{adenine}$, since the valence shell for the isolated Na^+, Mg^{+2} ions are empty $[E_{ion}$(valence electrons) $= 0]$. Net charge on the sodium never exceeds +1. All calculated points for the adenine + Na^+ thus fall within the range of the Hamiltonian matrix algorithm. The algorithm adopts a linear extrapolation procedure to determine the valence orbital ionization energies when the atomic net charges range from -1 to +1. The algorithm is no longer reliable when the magnitude of the net charge $|q| > 1$. We chose not to expand the range of reliability. Because of this, the bare Mg ion case presented some difficulties. The net charge for Mg along the solid line portion in Fig. 3 was ≤ +1. Over the dashed portion of the Mg-N1 curve, the net charge is greater than 1.1, and at 4.0 Å it equals +1.8. The energies of the Mg-N1 curve at 2.5 Å, 3.0 Å, and 3.5 Å were fitted to a quadratic equation form, $y = Ax^2 + Bx + C$, in order to determine the location of the minimum. Cramer's rule was used to solve the resulting set of

simultaneous equations. The extrapolated minimum and energy are 3.93 Å and -25.87 eV, respectively. The energy is smaller in magnitude than the energy associated with the Mg-N3 minimum. Therefore, the N3 site is predicted to be the favorable one for Mg^{+2}.

The preferred interaction site for the bare Na^+ is N1, which is in accord with Ref. [4]. The Mg case was not considered by these workers. The difference in energies between Na-N1 and Na-N3 when the Na^+ is at either minimum is roughly 0.08 eV (1.8 kcal/mole). This energy difference is consistent with the behavior of the Na-N1 and Na-N3 curves over the range of 2.5 Å to 3.5 Å. Reference [4] displays a difference of 2.4 kcal/mole. Our equilibrium distance, about 3.5 Å, is greater than the 2.15 Å value adopted in [4]. Energy differences between sites and general patterns for the adenine + Na^+ system agree remarkably well with [4].

The hydrated ion complex was constructed in the following manner: Four water molecules were tetrahedrally disposed about the ion (Na or Mg) with the oxygens placed at the vertices of the tetrahedron. The tetrahedral structure was chosen because it gives a "saturated" geometrical shape which is consistent with the experimentally deduced solvation numbers for Na and Mg [7]. Calculations involved only the simultaneous and equal dilation or contraction of distances between the ion and the four water molecules; that is, the tetrahedron was uniformly expanded or reduced in size. The equilibrium distance between the oxygen of the water molecules and the ion (at the center of the tetrahedron) was found to equal 2.4 Å for both Mg and Na using the modified IEH. This distance

is in good agreement with fits for Mg [7] and is in reasonable agreement with the _ab_ _initio_ calculations for Na^+ and a _single_ water molecule [8]. It is to be expected that some expansion in the solvation shell will occur when Na^+ is surrounded by four waters. One water was removed for the interaction between a hydrated ion and the adenine or thymine. The oxygens of the remaining three waters formed an equilateral triangle which served as the base of a triangular pyramid whose vertex was at the adenine N1 or N3, for example. Figures 4 and 5 typify the approach. The ion is in the plane of the adenine. The pathways bisect the angles (C2-N1-C6) and (C4-N3-C2). The water hydrogens were disposed so as to reduce interactions between various pairs, while also minimizing inter-action between these pairs and the adenine or thymine. The adenine results are displayed in Fig. 6. The net charge on the Mg was less than +1 at all distances considered. In both cases, $(Mg \cdot 3H_2O)^{+2}$ and $(Na \cdot 3H_2O)^+$, the N1 site is favored. In fact, the $Mg \cdot 3H_2O$-N3 curve is repulsive. The binding energies, $\Delta E_{bind} = E_{adenine \cdot ion \cdot 3H_2O} - E_{adenine} - E_{ion \cdot 3H_2O}$, are considerably reduced with respect to the adenine·ion binding energies. The pathway examined for $Mg \cdot 3H_2O$-N1 clearly is not an optimal one when $R \gtrsim 3.9$ Å, since the isolated $(Mg \cdot 3H_2O)^{+2}$ and isolated adenine system is more stable than the interactive one. The most important result is obtained when the displacement energies are combined with the binding energies. That is, we ask whether the adenine N1 or N3 nitrogens can displace a water from the ion·$4H_2O$ complex. The total energy difference

$$\Delta E_{displacement + binding} = E_{ion \cdot 3H_2O} + E_{H_2O} - E_{ion \cdot 4H_2O} + \Delta E_{bind},$$

$$= E_{H_2O} - E_{ion \cdot 4H_2O} + E_{adenine \cdot ion \cdot 3H_2O}$$

$$- E_{adenine}. \tag{3.1}$$

The results are compiled in Table 2 and show that ΔE is _positive_ for either Mg or Na. Treated as an equilibrium problem, the overall displacement plus binding reaction for N1, for example, has an "apparent" equilibrium constant

$$K(N1) = \frac{(adenine \cdot ion \cdot 3H_2O)_{N1}(H_2O)}{(adenine)(ion \cdot 4H_2O)} \simeq exp(-\Delta E_{displacement + binding}/kT). \tag{3.2}$$

At room temperature (300 K), the approximate value for this equilibrium constant when the reaction involves the hydrated Na ion equals

$$K(N1) \simeq 4.0 \times 10^{-31},$$

while the equilibrium constant, when the hydrated Mg ion is involved, equals

$$K(N1) \simeq 2.5 \times 10^{-45}.$$

Similar results are obtained with the hydrated Na ion for K(N3); however, since the magnesium complex $(Mg \cdot 3H_2O)^{+2}$ does not bind with the N3 site, the equilibrium constant $K(N3) = 0$, for all temperatures. Therefore, N1 or N3 will _not_ displace a water molecule from the complex $ion \cdot 4H_2O$; i.e., the displacement plus binding reaction does not oc : to any

significant degree. Hence, we expect that neither Na^+ nor Mg^{+2} will bind to the adenine N1 or N3 in an aqueous medium. There appears to be experimental confirmation with regard to the Mg^{+2}(aqueous) case [9].

3.2 Thymine

The results for thymine + ion are displayed in Fig. 7. Only the Na^+ results for approaches to O2 or O4 are presented. The Mg case is not displayed because the net charge on the magnesium was greater than +1.5 at all distances for either an O2 or O4 pathway. The energy algorithm, as noted in section 3A, breaks down when the net charge on an atom exceeds +1. In the Na^+ case, the O4 site is more stable than the O2 site by ca. 10 kcal/mole. Reference [4] finds the O4 site in uracil more stable than the O2 site by 4.2 kcal/mole. Binding to the ethylenic double bond (C5-C6) is highly unfavorable from our calculations. The curves labelled Mg-C = C, Na-C = C are repulsive. This is in agreement with Ref. [2] with respect to Mg^{+2}. Energy differences (e.g., $E_{Na-O4}-E_{Na-O2}$) agree more closely with Ref. [2] than do the separate magnitudes, which mirror the behavior found in the adenine case. The results are reversed when the ions are hydrated (see Fig. 8). That is, the O2 site becomes the favored site. This arises because of interactions between the waters and the methyl group attached to C5. Note that when the $Na \cdot 3H_2O$ and $Mg \cdot 3H_2O$ entities are sufficiently distant from the O2 and O4 sites (>3.0 Å for $Na \cdot 3H_2O$ and >3.4 Å for $Mg \cdot 3H_2O$), the O4 pathway is favored. It is also noteworthy that neither O2 nor O4 pathways are favorable for $Na \cdot 3H_2O$ at distances greater than 3.4 Å. Assuming that these repulsive regions are not artifacts of the method, it then

follows that it may not suffice to determine binding energies when eval-
uating the ease with which binding can be expected to occur, since the
repulsive regions favor the recombination of $(Na \cdot 3H_2O)^+$ with H_2O to form
$(Na \cdot 4H_2O)^+$. As with adenine, displacement and binding energies were
calculated. Results are presented in Table 2. Both sites, O2 and O4,
exhibit $\Delta E_{binding + displacement} < 0$. Thus, the thymine can displace a
water from the ion$\cdot 4H_2O$ complex. The prediction that O2 is a favored
site appears consistent with experimental evidence for Mg(aqueous) [9].

4. Discussion and Conclusion

Our results for adenine + Na^+ and thymine + (Na^+, Mg^{+2}) are in good
qualitative agreement with ab initio model work on adenine [4] and
uracil [2]. Energy differences between competing sites, where compari-
sons can be made, are in excellent agreement. Absolute energy magni-
tudes are not in agreement; these magnitudes roughly correspond to what
one might expect from CNDO. However, CNDO does fail when applied to
uracil (see Ref. [2]), while the Modified IEH results are in accord with
the conclusions drawn from the ab initio work. Thymine does differ from
uracil in that a methyl group replaces the C5 hydrogen; no differences,
with regard to steric effects, are to be expected with the bare ion
interacting with either the thymine or uracil. The water molecules of
the hydrated ions, on the other hand, do interact with the methyl group;
these interactions lead to O2 being the most favorable site rather than
O4.

No attempt was made to optimize any of the standard IEH parameters in
the systems studied. It is indeed gratifying that the results agree to

the extent that they do with both _ab_ _initio_ work on bare ions and experimental trends for hydrated ions. The Modified IEH allows inexpensive calculations to be performed on systems where standard IEH cannot be used at all, though experience with standard IEH remains a valuable guideline. Thus, we feel that the results obtained in this communication are sufficiently encouraging that one could hope to model other systems of experimental interest which might provide bridges to span the gap between theory and experiment.

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Table 1. Standard Extended Hückel parameters for H, C, N, O, Na, Mg

A. Basis set exponentials $(\text{Bohr radii})^{-1}$

H	$\zeta_{1s} = 1.0000$	
C[a]	$\zeta_{2s} = 1.6083$	$\zeta_{2p} = 1.5679$
N[a]	$\zeta_{2s} = 1.9237$	$\zeta_{2p} = 1.9170$
O[a]	$\zeta_{2s} = 2.2458$	$\zeta_{2p} = 2.2266$
Na[a]	$\zeta_{3s} = 0.8358$	$\zeta_{3p} = 0.8358$
Mg[a]	$\zeta_{3s} = 1.1025$	$\zeta_{3p} = 1.1025$

B. Valence orbital ionization energies, eV

	$M^+ \rightarrow M^{++} + (e)$	$M \rightarrow M^+ + (e)$	$M + (e) \rightarrow M^-$	
H[b]	−15.36	−13.60	−0.76	(1s)
C[b]	−31.65	−20.78	−8.89	(2s)
	−23.61	−11.32	−0.87	(2p)
N[b]	−39.99	−25.16	−13.80	(2s)
	−29.65	−14.16	−1.08	(2p)
O[c]	−47.84	−32.37	−19.24	(2s)
	−33.63	−15.86	−1.93	(2p)
Na[d]	−15.15	−5.09	+0.96	(3s)
	−10.74	−2.96	+1.81	(3p)
Mg[d]	−18.92	−7.60	+0.47	(3s)
	−14.29	−4.47	+1.40	(3p)

[a]Ref. [10], Table I.

[b]Ref. [11], Table 5.

[c]Ref. [12], Table I.

[d]Adopted from Ref. [13], Tables D.1, D.4.

Table 2.   Site binding and displacement energies for adenine and thymine interacting with hydrated Na^+, Mg^{+2} ions

Complex	Site	$R^{equilibrium}_{ion-site}$, Å	$\Delta E1^a$, eV (binding)	$\Delta E2^b$, eV (binding + displacement)
Adenine·Na·3H$_2$O	N1	3.0^c	−0.78	+1.82
	N3	3.0^c	−0.65	+1.96
Adenine·Mg·3H$_2$O	N1	3.5^c	−0.26	+2.67
	N3	----	NO BINDING	----
Thymine·Na·3H$_2$O	O2	2.5^c	−3.26	−0.65
	O4	3.0^c	−2.81	−0.21
Thymine·Mg·3H$_2$O	O2	2.5^c	−6.11	−3.17
	O4	2.5^c	−4.67	−1.74

$^a\Delta E1$ = E(adenine,thymine·ion·3H$_2$O) − E(adenine,thymine) − E(ion·3H$_2$O).

$^b\Delta E2$ = $\Delta E1$ + E(ion·3H$_2$O) + E(H$_2$O) − E(ion·4H$_2$O).

^{c}These values are reliable (within the context of the calculations) only to ± 0.3 Å.

FIGURE TITLES

Fig. 1. The adenine molecule

Fig. 2. The thymine molecule

Fig. 3. Potential curves (ΔE vs. R) for the bare Na^+, Mg^{+2} interacting with the N1, N3, N7 sites on adenine. The cations are brought in along paths which are in the plane of the adenine and which bisect the respective site angles C2-N1-C6, C2-N3-C4, C5-N7-C8. See text for description of dashed line

Fig. 4. Hydrated cation (three water molecules) approaching the N1 site on adenine. The oxygens of the water molecules are at the vertices of the equilateral triangle which forms the base of a pyramid involving N1. The apex of the pyramid is occupied by the site. One water is above the plane of the paper. The other two waters are below. The cation is 4.0 Å from the N1

Fig. 5. Hydrated cation (three water molecules) approaching the N1 site on adenine. Deployment of the waters is the same as in Fig. 4 except that the distance between the cation and the N1 site is 2.5 Å

Fig. 6. Potential curves (ΔE vs. R) for hydrated Na^+, Mg^{+2} approaching the N1, N3 sites on adenine. The paths are the same as those in the bare ion case

FIGURE TITLES, continued

Fig. 7.   Potential curves (ΔE vs. R) for the bare Na^+, Mg^{+2} approaching
the O2, O4 and the ethylenic double bond (C5-C6 in Fig. 2)
sites on thymine.   Paths are in the plane of the thymine and
are at 180 deg. with respect to C2-O2, C4-O4.   The path to the
ethylenic double bond disects the bond.   The numbers in paren-
theses along the Na-O4 curve is the calculated net charges on
the Na

Fig. 8.   Potential curves (ΔE vs. R) for the hydrated (three water
molecules) Na^+, Mg^{+2} approaching the O2 and O4 sites on thymine.
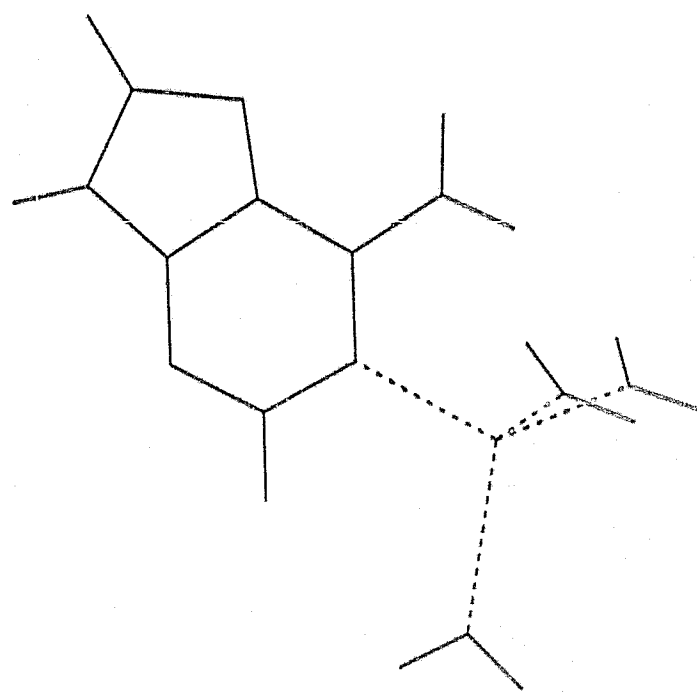Paths are identical to the bare ion case
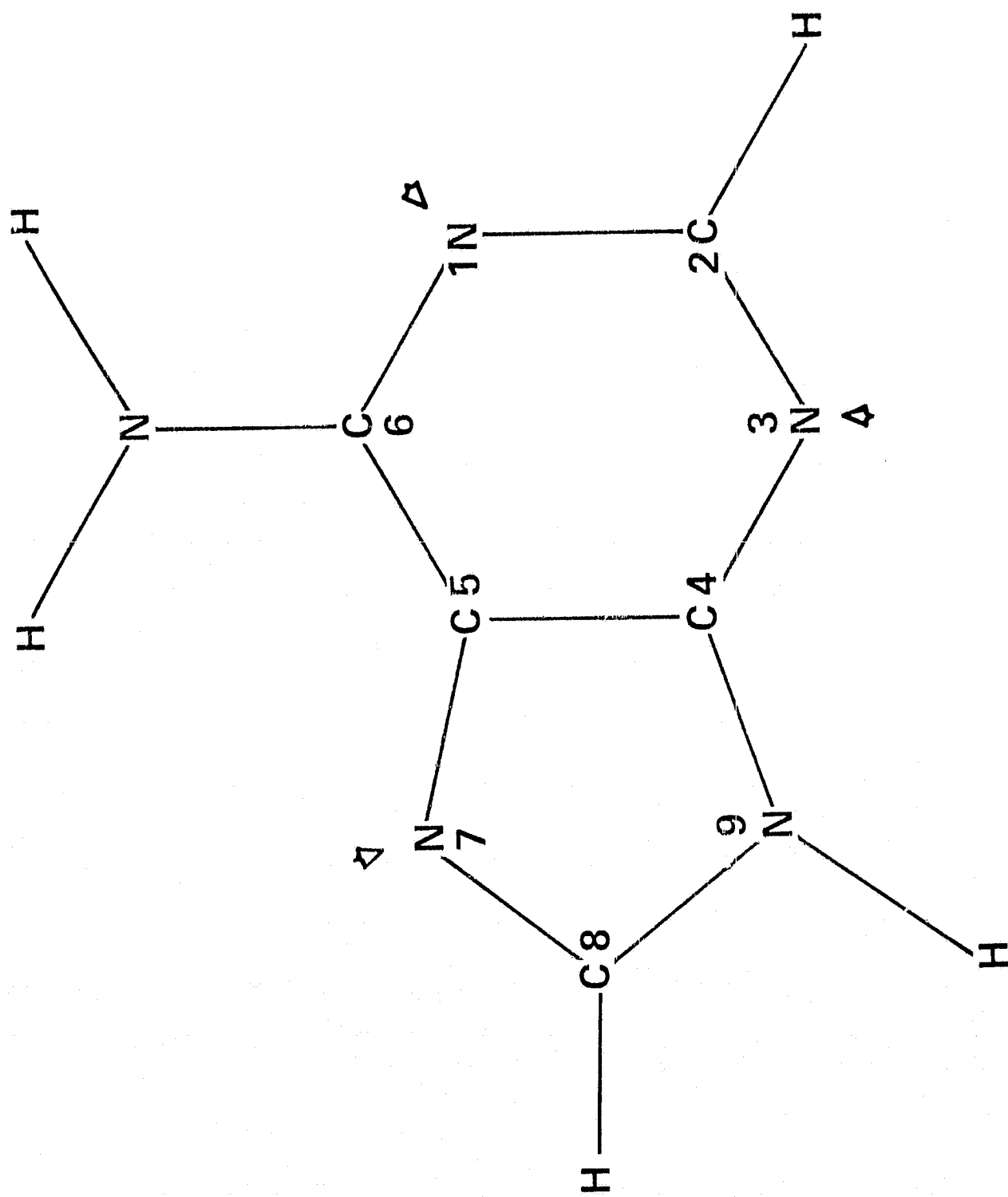
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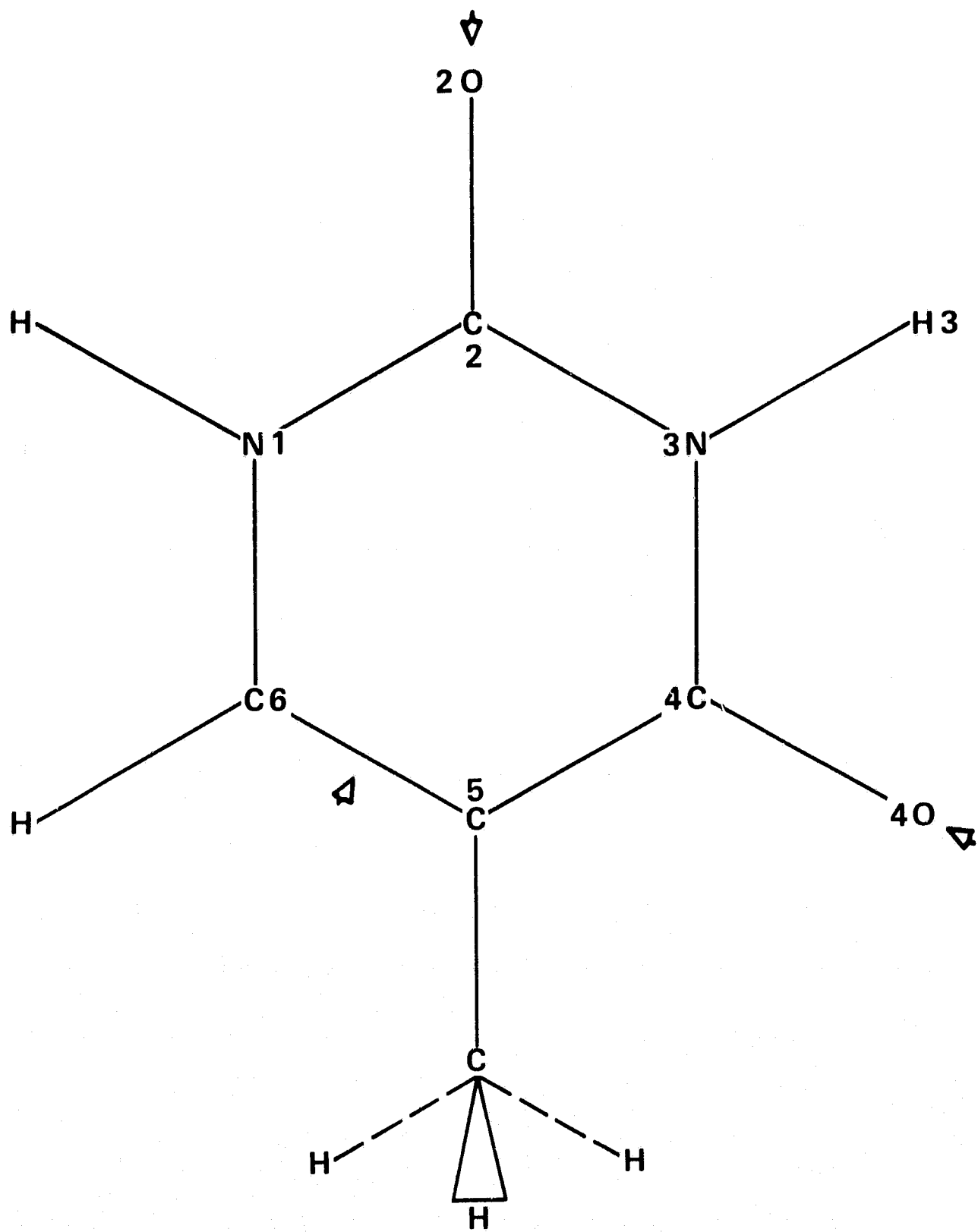
Fig. 2
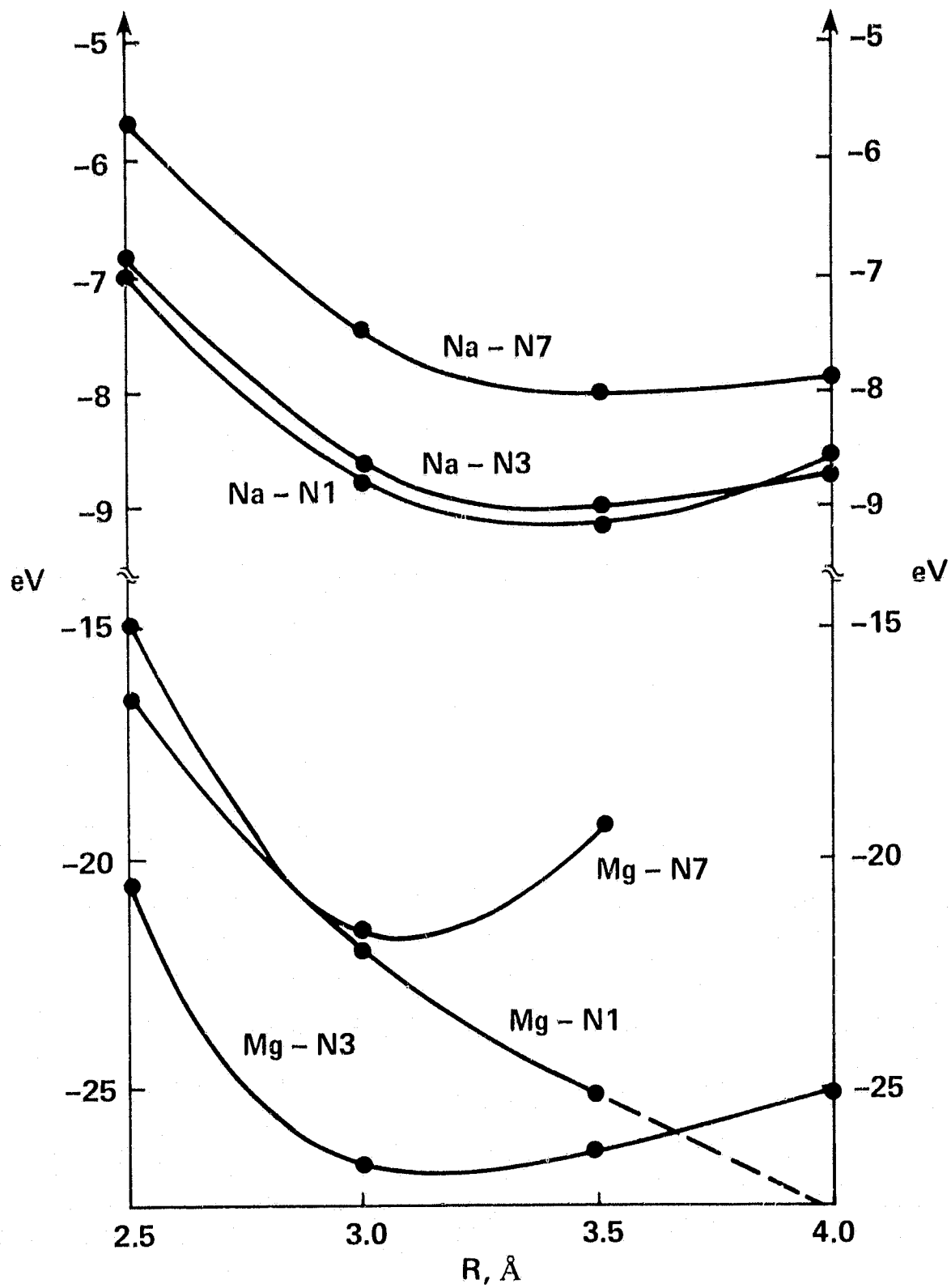
Fig. 3

Fig. 4

Fig. 5

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Fig. 7

Fig. 8