constants in Table I. The quantity α refers to the mole fraction of glutathione present at the stage of ionization indicated by the subscripts, where the subscripts are used in the same manner as with the microscopic constants. These calculations reveal that at the physiological pH of 7.4, the sulfhydryl proton is ionized in 2.8% of the glutathione.

This study represents the first part of a program directed toward characterizing the acid–base chemistry of amino acids and peptides at the molecular level. The microscopic ionization constants of glutathione and methylmercury-complexed glutathione were determined directly from chemical shift data without the use of macroscopic constants. The methods developed for evaluating the data are applicable to polyprotic systems in which the fractional ionization of each of the acidic groups undergoing simultaneous ionization can be determined as a function of pH. We are presently investigating the application of proton and carbon-13 nmr to the quantitative characterization of the acid–base chemistry of other amino acids and peptides.

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Electronic Spectra of Nucleic Acid Bases. I. Interpretation of the In-Plane Spectra with the Aid of All Valence Electron MO–CI Calculations

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Abstract: The in-plane part of the electronic spectra of nucleic acid bases as well as of their tautomers and ions is assigned by means of all valence electron SCF–MO–CI calculations. The various transitions of different bases are correlated using the nodal properties of the excited states. The spectra of pyrimidine and purine bases can both be divided into two groups, namely the cytosine and uracil type and the adenine and hypoxanthine type. Structurally, bases which show uracil or hypoxanthine type spectra differ from those which show cytosine or adenine type spectra by an additional proton at one of the nitrogen atoms of the six-membered ring. In pyrimidine bases, the presence of this proton leads to an increase in intensity of the transition lowest in energy and a decrease in intensity and shift toward higher energy of the second to lowest. The nodal patterns of both transitions are still similar in cytosine to those of pyrimidine, whereas in uracil they resemble more those found in an α,β-unsaturated ketone. In purine bases the excited states are more similar to those of purine itself but distinctly different from those of the underlying indole system. Adenine-type spectra are characterized by the fact that the lowest transition is localized mainly at N7=C8 in the five-membered ring, whereas the second spreads out over the fragment C2=N3—C4=C5—N7=C8 and corresponds to the lowest transition in a triene. In hypoxanthine-type spectra these two transitions are interchanged. Protonation at N7 in the five ring reverses this change and leads back to adenine-type spectra. We can exclude on the basis of our calculated spectra the possibility that protonation of adenine occurs at N7. The usual assumptions about the most stable tautomers are confirmed by a comparison of calculated and measured spectra. The results of the present calculation show that not only $n \rightarrow \pi^*$ transitions, but also $\pi \rightarrow \pi^*$ transitions, are profoundly affected by protonation and tautomerization. Hydrogen bonding in crystals might have a similar though smaller effect.

There have been numerous attempts to understand and correlate the electronic spectra of nucleic acid bases both experimentally[1–19] and theoretically.[20–30] The spectra of these compounds are of interest in themselves; furthermore, their understanding is necessary

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for successful prediction and interpretation of the uv and CD spectra of nucleic acids.

Experimental approaches comprise such different techniques as empirical correlation of absorption bands and their shift with solvent variation,[1,2] film spectra,[4,5] fluorescence[6,7] and phosphorescence[8,9] spectra, crystal absorption[10-12] and reflection[13-15] spectra, polarized stretched film spectra,[16] electrochromism measurements,[17] and the use of CD and MCD techniques.[18,19] There is thus a great deal of very useful data on the spectra of nucleic acid bases and their changes with ionization and environment. However, a general understanding is still lacking.

Theoretical treatments have thus far been limited to the π electrons,[20-29] or, at most, to one-determinantal descriptions of excited states including all valence electrons.[30,31] The π-electron calculations do not consider the polarization of the σ core, which is obviously important in molecules containing several different heteroatoms, and they can of course not account for out-of-plane transitions. One-determinantal MO approaches have met with little success in reproducing the spectra of aromatic compounds. A one-determinantal description of the excited states of, *e.g.*, benzene, is qualitatively insufficient. Nucleic acid bases are compounds of at least comparable complexity.

We have therefore considered it worthwhile to calculate the spectra of nucleic acid bases, their tautomers, and ions, with an all valence electron SCF–MO method that includes configuration interaction for the excited states.[32] In general, the results obtained are good in qualitative and even quantitative respects. Yet, it should not be overlooked that the calculation is still a very crude approximation. However, our primary goal is less the reproduction of experimental facts than the ordering of a variety of experimental data in a common scheme.

In paper I of this series we deal with the in-plane part ($\pi \rightarrow \pi^*$, $\sigma \rightarrow \sigma^*$ transitions) of the spectra. In paper II we will discuss the out-of-plane part (n $\rightarrow \pi^*$, $\pi \rightarrow \sigma^*$ transitions). Very little is known about out-of-plane transitions in nucleic acid bases, in particular with regard to the energetic splitting between n $\rightarrow \pi^*$ transitions.[32] It will be shown that for nucleic acid bases the energy gaps between different n $\rightarrow \pi^*$ transitions are considerable.

Calculations

CNDO–CI Method. The CNDO method,[33] with a description of the excited states by a linear combination of singly excited configurations,[34] seems to be well suited for our purpose. All valence electrons are included in the calculation, and the out-of-plane as well as the in-plane transitions in nucleic acid bases can be accounted for. As a basis set we use 1s orbitals for hydrogen atoms and 2s,2p Slater orbitals for atoms of the first row. The singly excited configurations are obtained by using the virtual orbitals of the ground-state calculation. The 120 configurations which are lowest in energy are used. Details about the parametrization, which was recalibrated using mainly the spectrum of uracil and *s*-tetrazine, are found in the Appendix.

The CNDO method enables us to calculate the singlet spectra of rather large molecules with a relatively small amount of computer time. The ZDO (zero differential overlap) approximation eases the extraction of pictorial information from MO wave functions. Connected with these advantages are some limitations which have to be kept in mind. First, results for triplet spectra are often poor because some of the terms leading to the splitting of singlet and triplet states are neglected.[35] Second, n $\rightarrow \pi^*$ and $\pi \rightarrow \sigma^*$ transitions do not mix for similar reasons. It can easily be seen that the corresponding off-diagonal elements[36] of the configuration interaction matrix vanish within the CNDO approximation. Admixing of $\pi \rightarrow \sigma^*$ configurations is hardly important for n $\rightarrow \pi^*$ transitions at low energies but might get serious in regions where both types of configurations lie closer together. And third, our parametrization and basis set account for valence electron transitions but not for transitions having preponderant Rydberg character.[37] For these reasons we have limited our calculations to the 15 lowest singlet states and discuss only those in detail which appear below about 48 kK.

Calculated Spectra. For the presentation of our data we use calculated line spectra together with the measured uv spectra and spectra which we calculate by assuming Gaussian shapes for the absorption curve of the individual transitions. For the half-width ($\Delta\tilde{\nu}_i$) of the Gaussians a value of 2.5 kK was chosen for all transitions as no systematic trend[38] for the band width in the experimental spectra of nucleic acid bases was evident. The absorptivities are calculated according to

$$\epsilon(\nu) = 51.15 \sum_i \frac{\mu_i^2 \tilde{\nu}_i}{\Delta\tilde{\nu}_i} \exp \frac{-0.69(\tilde{\nu} - \tilde{\nu}_i)^2}{\Delta\tilde{\nu}_i^2} \qquad (1)$$

with μ_i in Debyes and $\tilde{\nu}_i$ in kK (= 1000 cm^{-1}). We have scaled the calculated absorptivities by a factor of 0.35. For the calculation of transition moments we used the length form of the dipole operator within the ZDO approximation.[33] As usual when applying the length form to approximate wave functions, dipole strengths and in turn the calculated absorptivities are too high.[39] As the relative intensities of the transitions are correct, this does not affect the conclusions which are based on them. Transition moments calculated in the ZDO approximation differ from those obtained using transition monopoles (see next section) by the inclusion of local polarization terms, *i.e.*, terms of the form $\langle s|r|p\rangle$.

In comparing measured and calculated directions of transition moments a few often overlooked precautions should be observed. The dipole operator belongs to

(31) For thymine a nonempirical LCAO–SCF calculation with a minimum set of atomic basis functions approximated by Gaussians has been performed. CI for excited states was limited to four configurations, and the calculated single-singlet excitation energies agree within 2–3 eV with observed ones; see L. C. Snyder, R. G. Shulman, and D. B. Neumann, *J. Chem. Phys.*, **53**, 256 (1970).

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the class of unbounded operators.[40] This means that large errors for $\langle r \rangle$ cannot be excluded even for quite accurate wave functions.[41] This is probably particularly true for calculated directions of transition moments in molecules devoid of higher symmetry. The influence of the ZDO approximation in this respect has not yet been investigated.

A very important approximation present in all calculations of polyatomic molecules regardless of the degree of sophistication is the Born–Oppenheimer approximation. Transitions calculated to be weak but lying near intense transitions may not only exhibit considerable intensity but also very different measured directions, due to vibronic mixing.

Measured absolute directions of transition moments are obtained mostly from crystal absorption or reflection spectra. They suffer from the fact that changes due to interactions in the crystals cannot be accounted for accurately. Approximate corrections for these changes have led to alterations of angles of 15°.[13] Relative directions obtained by different methods are sometimes in disagreement too, for the two longest wavelength in-plane transitions of 9-ethylguanine for instance by nearly 20°.[15,16] Bases, on which measurements of transition moment directions are performed, in general carry substituents which prevent tautomerization or lead to favorable crystal structures, whereas our calculated directions are obtained for unsubstituted bases.

Nodal Properties of Excited States. Nucleic acid bases belong to the point group C_s and have a mirror plane which contains all the atoms of the molecules. Based on group theory we can therefore distinguish excited states which are symmetric with respect to this plane (a′) and give rise to in-plane transitions and states which are antisymmetric (a″) and lead to out-of-plane transitions. Unfortunately, no other rigorous subdivision is possible.

To identify electronic states according to their transformation properties under the symmetry operation of a point group, we actually use the nodal properties of their wave functions. We can try to carry on the principle of classifying states according to their nodal properties and see if we can find common patterns for states, say, in different purine bases. This is indeed likely to occur. Though symmetry is of a discrete nature and arguments based on it break down upon its violation, chemistry is not. Arguments based on topological similarities rather than on symmetry alone are therefore often more generally applicable. In subsequent paragraphs we will show that using nodal properties of excited states is a very useful principle for classifying them in molecules devoid of symmetry, in particular because it is of a qualitative rather than a quantitative nature. In addition, the use of nodal properties might lead to general rules for the sign of rotatory strengths of the various transitions in bases chirally perturbed by substituents (analogous to the octant rule for ketones[42]).

To get an approximate measure for the nodes within the CNDO scheme, the concept of transition monopoles[43] seems to be well suited. For a single electronic transition $\mu \rightarrow \nu$ the wave function $\phi_{\mu\nu}$ is given by

$$\phi_{\mu\nu} = \frac{1}{\sqrt{2}}\{|\varphi_1\bar{\varphi}_1 \ldots \varphi_\mu\bar{\varphi}_\nu \ldots \varphi_n\bar{\varphi}_n| - |\varphi_1\bar{\varphi}_1 \ldots \bar{\varphi}_\mu\varphi_\nu \ldots \varphi_n\bar{\varphi}_n|\}$$

with the molecular orbitals $\varphi_\mu = \sum_{q=1}^{2n} c_{q\mu}\chi_q$. χ_q are the atomic basis functions and $c_{q\mu}$ the MO coefficients. The value of the transition monopole $Q_A{}^{\mu\nu}$ at atom A is

$$Q_A{}^{\mu\nu} = \sqrt{2}\sum_{q(A)} c_{q\mu}c_{q\nu}$$

where $q(A)$ indicates summation over the atomic orbitals χ_q located at atom A.

For an excited state Φ, given by a sum of singly excited configurations

$$\Phi = \sum_{\mu,\nu} B_{\mu\nu}\phi_{\mu\nu}$$

we get

$$Q_A = \sum_{\mu,\nu} B_{\mu\nu}Q_A{}^{\mu\nu} \qquad 1 \leq \mu \leq n,\ n+1 \leq \nu \leq 2n$$

For the representatives of the different types of spectra of nucleic acid bases we have depicted the monopoles Q in a pictorial way. The magnitude of Q_A is indicated by the size of the circle located at atom A and the sign by the circle being filled or not.

The General Feature of the In-Plane Spectra. The in-plane transitions largely determine the gross appearance of the uv spectra of all the nucleic acid bases and their polymers. Probably, the interactions of these transitions are the most important terms determining the CD spectra of polymers but not necessarily of mononucleotides. In our calculation, the in-plane transitions are composed of $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$ configurations, the latter mainly $n \rightarrow \sigma^*$. For lower energies, say less than 48 kK (210 nm), the $\pi \rightarrow \pi^*$ contributions prevail by far. The transitions of lower energy can therefore be discussed neglecting contributions from hydrogen atoms.

A promising approach[2] to correlate the in-plane spectra of the different bases has been to start with the unperturbed pyrimidine chromophore, whose spectrum can be related to that of benzene. Our calculation shows that the perturbation of the pyrimidine chromophore is in general strong enough to make a different approach more useful. We divide the spectra of pyrimidine and purine bases both in two groups, namely the cytosine (C-type) and uracil (U-type) spectra and the adenine (A-type) and hypoxanthine (H-type) spectra. Nevertheless, important insight can be gained for the spectra of pyrimidine bases by relating them back to that of benzene by means of their monopole pattern.

Spectra of Pyrimidine Bases. The main characteristics of the spectra of cytosine and uracil are collected in Table I. Both bases have *two* in-plane transitions labeled I and II in the range 35–48 kK (285–210 nm). In pyrimidine the corresponding transitions appear at 41 kK (243 nm) and 47 (212) and correspond to the B_{2u} and B_{1u} states in benzene which are found at similar energies.

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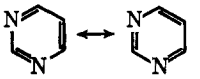
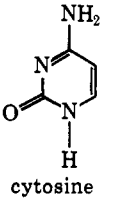
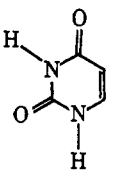
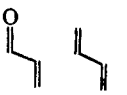
Table I. Spectral and Structural Characteristics of Cytosine and Uracil

		 pyrimidine	 cytosine	 uracil		
	D_{6h}	C_{2v}	C_s	C_s	C_s	C_{2h}
	Increasing localization of π electrons; decreasing aromaticity →					
I		ϕ_{calcd} 30°	18°	−8°		
		B_1 E_{calcd} 44 kK	38 kK	40 kK		
	B_{2u}	E_{exptl} 41 kK	36 kK	39 kK		B_u
	Localization increases; intensity increases; energy increases →					
II		ϕ_{calcd} −60°	24°	12°		
		A_1 E_{calcd} 45 kK	47 kK	51 kK		
	B_{1u}	E_{exptl} 47 kK	43 kK	?		A_g
		Energy increases; intensity decreases →				
III		ϕ_{calcd} −60°	−45°	−67°	First of a series of fairly intense transitions at higher energy	
		A_1 E_{calcd} 56 kK	53 kK	54 kK		
	E_{1u}	E_{exptl} ~55 kK	~49 kK	~49 kK		

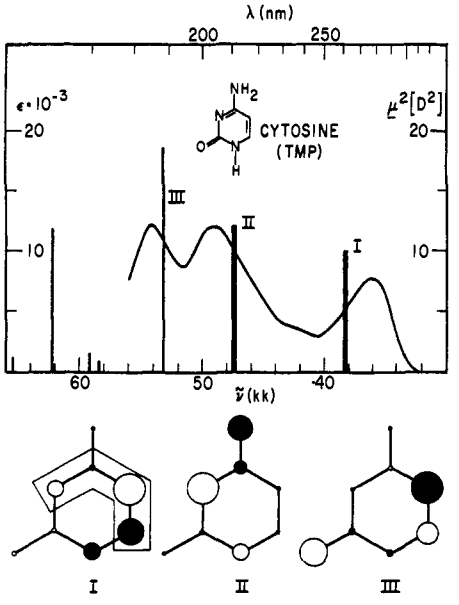
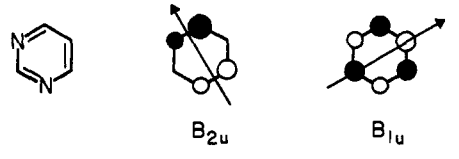
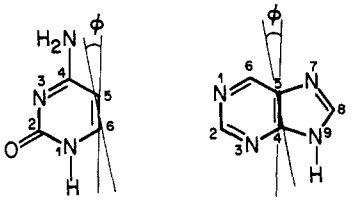


Figure 1. The spectrum of cytosine in TMP (trimethyl phosphate) with the calculated in-plane transitions and their monopoles.



In *cytosine* the transitions I and II are shifted toward lower energy and observed at 36 kK (275 nm) and 43 (235). From the transition monopoles of Figure 1 it can be seen that transition I in cytosine differs from I in pyrimidine mainly by the presence of a strong component along the formal double bond C5=C6. Along the fragment N3=C4—C5=C6 its nodal pattern corresponds to that of the lowest transition in a cisoid diene. (See Figure 5 for an actual comparison of nodal properties; the local chromophores of the bases are selected according to the size of the monopoles and their usefulness of correlating them to chromophores of known electronic structure.) Due to these changes a rotation of the transition moment in a clockwise direction takes place. Using the DeVoe–Tinoco convention[44] depicted below, this corresponds to a *decrease* of the angle ϕ. Transition II shows qualitatively the same monopole contributions as found in pyrimidine except for C5, but the exocyclic nitrogen substituent contributes a strong component, too. This clearly leads to an *increase* of ϕ. Therefore, transitions I and II in cytosine are no longer perpendicular but tend to get aligned roughly along C5=C6. The calculation of the excited states of 2-hydroxypyrimidine in the keto form has led to results for ϕ and the transition monopoles intermediate to those of pyrimidine and cytosine. This supports our conclusions. Experimentally, the transition moment directions of I and II are found to be nearly paralleled in cytosine.[14]



In *uracil* the only endocyclic double bond present is conjugated with the carbonyl group which replaces the amino group of cytosine. This leads to a marked increase and localization of the monopoles of transitions I and II along the acrolein like fragment C6=C5—C4=O (Figure 2). The deviations from a pyrimidine like pattern have become so large that it is better to consider I and II as being the two lowest excited states of an α,β-unsaturated ketone, perturbed by those of the urea part of uracil. (Alternatively, one might include N1 in the local chromophore, which then cor-

(44) H. DeVoe and I. Tinoco, Jr., *J. Mol. Biol.*, 4, 500 (1962).

responds to a vinylogous amide, the simplest case of a merocyanine dye, instead of an α,β-unsaturated ketone.) The nodal properties of I and II are fully consistent with this view. In the observed spectrum transition I occurs at 39 kK (258 nm). The calculated result for II is 51 kK (195 nm). If we assume that the calculated and observed energies of II differ by a similar amount for uracil as found for cytosine, we would expect II to appear at about 48 kK (210 nm), *i.e.*, at the red edge of the intense transitions observed at 50 kK.

The higher energy of transitions I and II in uracil as compared to cytosine can be understood in terms of the decreased interaction of the excited states of the urea and acrolein part of the molecule. The increasing localization of the π electrons in different parts of the ring in the series benzene–pyrimidine–cytosine–uracil corresponds to a decrease in aromaticity. Nmr data for ring currents found in cytosine and uracil parallel our findings.[45] Platt has introduced the concept of the round field and long field type of chromophores.[46] The round field type is represented in our calculations by benzene and to a lesser extent pyrimidine. Configuration interaction is here of prime importance and leads to a pair of forbidden or weak transitions at low energy and a pair of strong transitions at higher energy. In the long field case, configuration interaction becomes less important and the intensity difference between the two pairs of transitions disappears. Cytosine can be considered an intermediate case with the two lowest transitions of intermediate intensity. Uracil more clearly belongs to the long field category. In the calculation, the importance of the configuration interaction is decreased; the observed and calculated intensities of the lowest energy band are increased. The changes in the absorption intensities and in particular the much higher intensity of transition I as compared to II in uracil can also be understood directly as a consequence of their localization along the acrolein fragment of the molecule; the symmetric counterpart to *trans*-acrolein is a diene of point group symmetry C_{2h}. The lowest excited $\pi \rightarrow \pi^*$ state transforms according to B_u and is electric dipole allowed; the second transforms according to A_g and is forbidden. The direction of the transition moment of the intense transition I (Table I) agrees well with the experimental values of 0 or $+7$[12] and $-9°$[47] obtained for 1-methyluracil.

Spectra of Purine Bases. The conjugated system underlying purine is that of indole. Indole shows three transitions in the range 35–48 kK, calculated at 36 kK (278 nm) with a dipole strength of 4.8 D^2, 40 kK (252 nm, 3.1 D^2), and 48 kK (210 nm, 18.8 D^2), which can be related to those of benzene. Purine bases show also *three* transitions, I, II, and III in this range, but their nodal properties as well as dipole strengths are rather different from those of indole. A meaningful correlation with the excited states of benzene or pyrimidine is therefore not possible. This shows that the topological arrangement of the double bonds and that of all the heteroatoms in the purine system are equally important in determining the characteristics of excited states. We therefore have to consider purine itself as the basic system.

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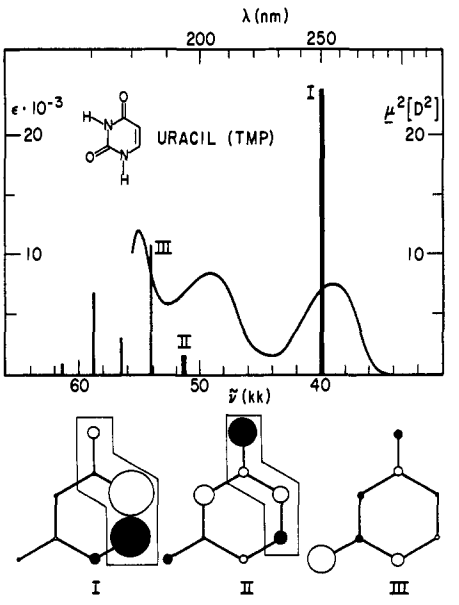
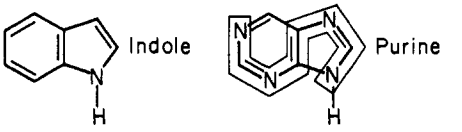


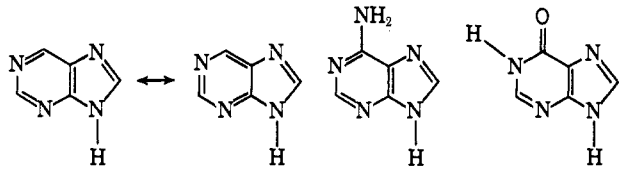
Figure 2. The spectrum of uracil in TMP with the calculated in-plane transitions and their monopoles.



Of the three excited states (I, II, and III) in purine bases, III lies highest in energy in the adenine as well as hypoxanthine type spectra. Transition III invariably shows the smallest and I the highest calculated dipole strength. The relative positions of I and II depend on whether one of the nitrogen atoms of the six ring carries a proton (H-type spectrum) or not (A-type spectrum). In the A-type spectra transition I lies lowest and in the H-type spectra transition II does (Figures 3 and 4 and Table II). Attachment of a proton at N7, *i.e.*, protonation of the five-membered ring, has the opposite effect of protonation of the six-membered ring and leads to A-type spectra with transition I lowest.

Transition I is characterized by the preponderant localization of the transition monopoles in the five-membered ring along the formal double bond N7=C8. *Transition II* spreads out over both rings, mainly along the triene fragment C2=N3—C4=C5—N7=C8. The nodal pattern along this fragment corresponds indeed exactly to those of the first excited state of a triene, as can be easily derived by a Hückel type argument (Figure 5). Under the point group symmetry C_{2h} of a corresponding symmetric triene, this transition would transform according to B_u and therefore be electric dipole allowed. The cis–trans–cis arrangement leads, however, to an extensive cancellation of the moment along the central C4=C5 double bond with those of the attached N=C groups. In our calculations the remaining moment of II is often directed roughly from one end of the triene chromophore to the other (C_2—C_8), but we can easily see that relatively small perturbations can affect the direction and intensity of transition II considerably. *Transition III* can be viewed in a similar way as II. According to its monopoles along the triene fragment, it clearly corresponds to the second $\pi \rightarrow \pi^*$ transition in a triene. In a triene belonging to the point

Table II. Spectral and Structural Characteristics of Adenine and Hypoxanthine[a]

						Nodal properties correspond to
		 purine adenine hypoxanthine				
		Increasing localization of π electrons of the six ring; decreasing aromaticity				
I		ϕ_{calcd}	50°	45°	37°	$\pi \rightarrow \pi^*$ transition in a monoene with some triene character in purine and adenine
		E_{calcd}	39 kK	39 kK	40 kK	
		E_{exptl}	38 kK	39 kK	40 kK	
		Increasing localization in the five ring; increasing energy; decreasing intensity				
II		ϕ_{calcd}	−57°	−45°	−71°	First $\pi \rightarrow \pi^*$ transition in a triene
		E_{calcd}	42 kK	41 kK	34 kK	
		E_{exptl}	42 kK	<42 kK	36 kK	
		Decreasing energy; increasing intensity				
III		ϕ_{calcd}	21°	29°	15°	Second $\pi \rightarrow \pi^*$ transition in a triene
		E_{calcd}	46 kK	45 kK	43 kK	
		E_{exptl}	?	?	(43 kK)	
		Decreasing energy; increasing intensity				
IV	First of a series of fairly intense transitions at higher energy	ϕ_{calcd}	−42°	−69°	40°	
		E_{calcd}	54 kK	54 kK	53 kK	
		E_{exptl}	50 kK	~49 kK	~51 kK	

[a] The heavy double bonds illustrate the pattern of excitation.

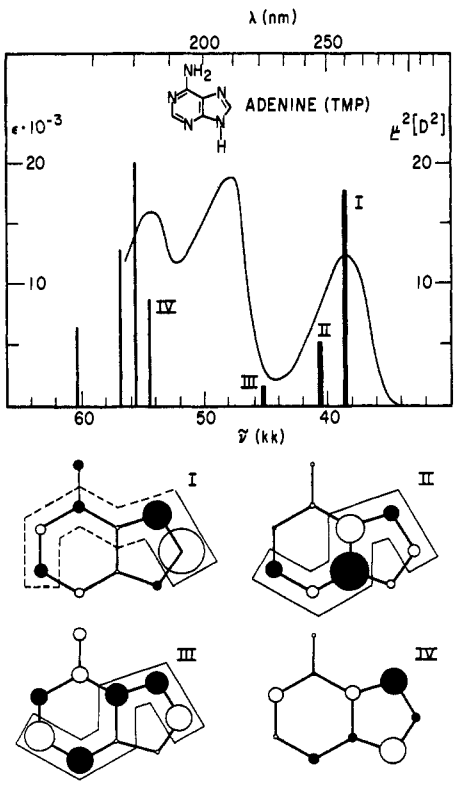


Figure 3. The spectrum of adenine in TMP with the calculated in-plane transitions and their monopoles.

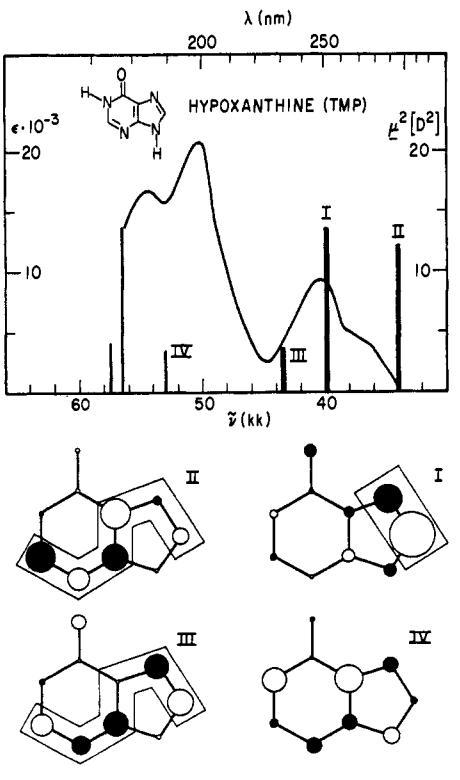


Figure 4. The spectrum of hypoxanthine in TMP with the calculated in-plane transitions and their monopoles.

group C_{2h}, this transition would transform according to A_g and therefore be electric dipole forbidden. This gives us an explanation for the consistently lower intensity and higher energy of III as compared to II and I.

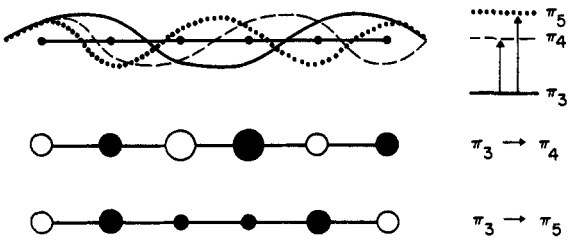


Figure 5. The nodal properties of the first and second $\pi \rightarrow \pi^*$ transition in a triene. A small shift of the position of the nodes of π_4 or π_5 due to lower symmetry can change the sign of the two middle monopoles for the second transition as observed for some purine bases.

Individual In-Plane Spectra

The calculated and the available experimental spectra of pyrimidine and purine bases, their tautomers, and ions fit into the scheme of four basic types of spectra presented above. The only restriction with respect to tautomerization which we have kept is the assumption that N1 in pyrimidine bases and N9 in purine bases carry a substituent, represented in our calculations by a hydrogen atom.

Calculated energy and intensity shifts are consistent with observed ones where a direct comparison is possible. However, for ions precise geometrical parameters are mostly lacking. We have, therefore, used essentially the same geometry for ions as we did for neutral species[48] and adjusted only exocyclic bonds. Infrared studies[49] have shown that this is a poor assumption and that the ring system undergoes sizable changes upon protonation and deprotonation. We have found that this affects calculated spectra more than changes in exocyclic bonds.

Bases with Cytosine-Type Spectra. Besides cytosine itself the *anion* and the *enol* of *uracil*, which both lack a proton at N3, are calculated to have C-type spectra (Figure 6). In the series uracil, uracil anion, and uracil enol the lowest energy transition decreases in intensity. Transition II increases and is shifted toward lower energy. Experimentally a decrease of 20% is found for I and a shoulder appears at 44 kK (225 nm; calcd 44 kK) when the pH of a solution of uridine is raised from neutral to 12 (Figure 7).

Bases with Uracil-Type Spectra. The *cation of cytosine* and the *imine* both carry a proton at N3. The calculated spectra are in accord with our generalization that this should lead to U-type spectra. The intensity of I increases in the series cytosine, cytosine cation, and cytosine imine. Transition II decreases and is shifted toward higher energies (Figure 6). For cytidine at pH 2.5 an intensity increase of 45% is observed for the lowest transition (Figure 7). In our calculation the transitions at higher energy merge and we can therefore not decide if II is the only in-plane component of the experimental peak found at 48 kK (210 nm; calcd 48 kK) or not.

We did not calculate the spectrum of *thymine* but its observed spectrum and its structure clearly place it in the U-type category.

Bases with Adenine-Type Spectra. *Purine* is the simplest base which lacks protons on the nitrogen atoms

(48) M. Spencer, *Acta Crystallogr.*, **12**, 59 (1959).
(49) M. Tsuboi, Y. Kyogoku, and T. Shimanouchi, *Biochim. Biophys. Acta*, **55**, 1 (1962).

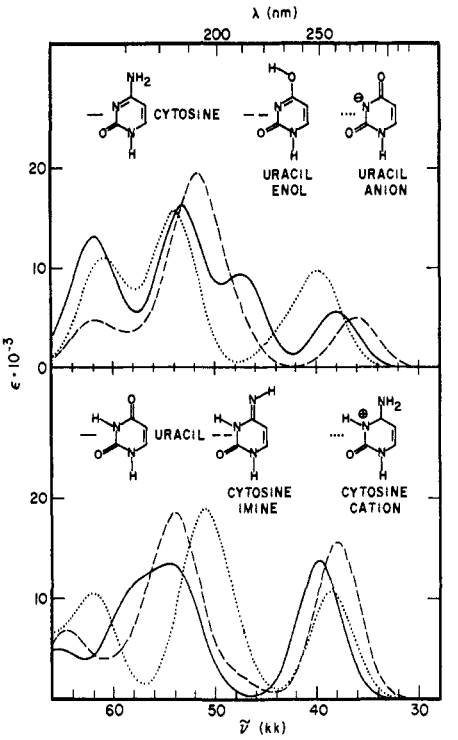


Figure 6. C-Type spectra (above) and U-type spectra (below) calculated with the 15 lowest in- and out-of-plane transitions. The half width is 2.5 kK for all transitions.

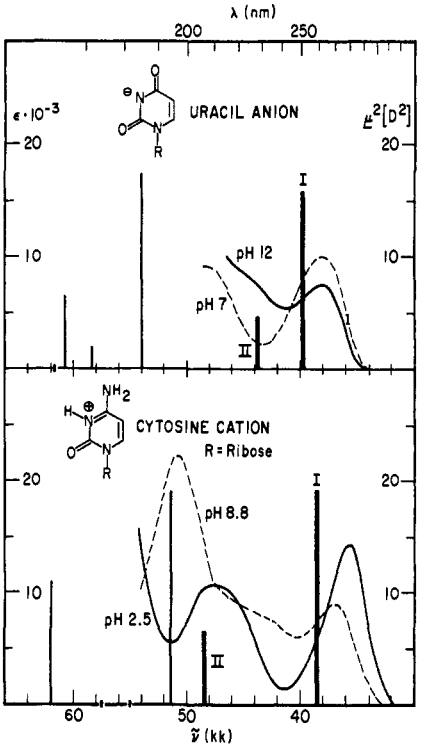


Figure 7. The spectrum of uridine at pH 7 and 12 (above) and of cytosine at pH 8.8 and 2.5 (below) with the calculated in-plane transitions for the anion of uracil and cation of cytosine.

of the six ring and therefore exhibits an A-type spectrum (Figure 8). We could have labeled this type of spectrum equally well after purine but choose an actual nucleic acid base for the sake of consistency. In purine, transitions I, II, and III are calculated to be less intense

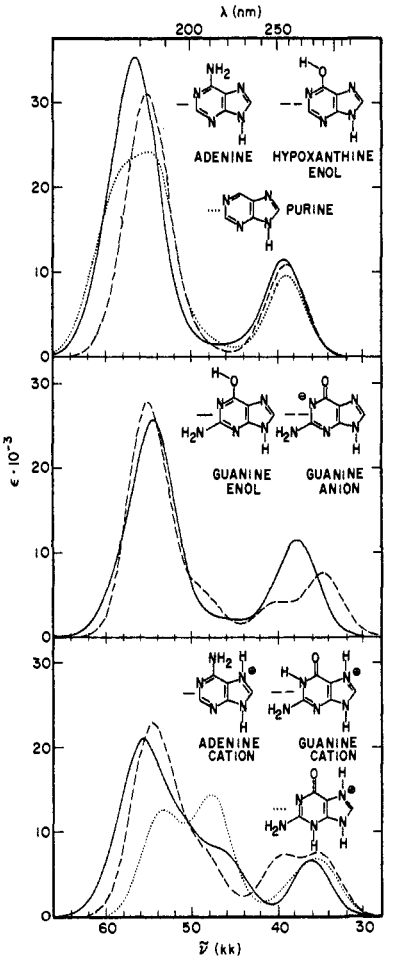


Figure 8. The A-type spectra of purine bases calculated with the 15 lowest in- and out-of-plane transitions. The half width is 2.5 kK for all transitions.

and II and III to be shifted slightly toward higher energy as compared to adenine. The measured spectra of purine (Figure 10) and adenine (Figure 3) confirm the calculations; II shows up clearly in purine as a shoulder at 42 kK (238 nm; calcd 42 kK), whereas in adenine II is hidden by I. The presence of a weak second transition at the high energy side of I has also been inferred from polarized fluorescence measurements in adenine[6] and from crystal absorption spectra.[10] In both compounds, III probably lies at the red edge of the several intense transitions appearing at higher energy.

The *enol of hypoxanthine* is the molecule which resembles adenine closest, structurally as well as with respect to its calculated spectrum. The spectrum of 6-methoxypurine is known (Figure 10) and presumably represents a good substitute for the unknown spectrum of the enol of hypoxanthine. The spectral changes observed and predicted for the keto–enol tautomerism of hypoxanthine provide therefore an interesting test case for the individual calculations as well as for our generalizations. Our scheme predicts that the low energy shoulder observed for the keto form at 36 kK (275 nm in TMP, Figure 4) must be absent in the spectrum of the enol because transition II should now lie at the high-energy side of transition I. This is indeed observed for 6-methoxypurine. In addition, the 40-kK (250 nm) absorption peak is skewed in the opposite direction.

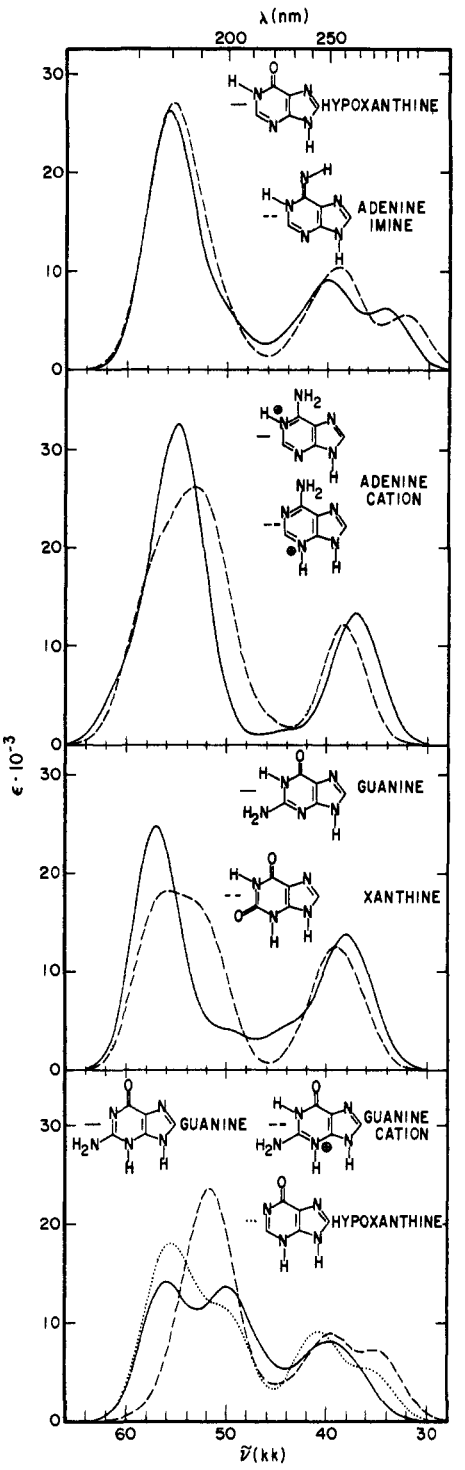


Figure 9. The H-type spectra of purine bases calculated with the 15 lowest in- and out-of-plane transitions. The half width is 2.5 kK for all transitions.

We did not calculate the spectrum of the *anion of hypoxanthine*. According to its structure, it should exhibit an A-type spectrum. The experimental data[2] for 9-methylhypoxanthine upon raising the pH are in full agreement with this conclusion.

The *enol of guanine* differs structurally from the enol of hypoxanthine by an additional amino group in the 2 position. In the calculated results the main change is an increase in intensity of the spectrum (Figure 8). Experimental data are not available for comparison.

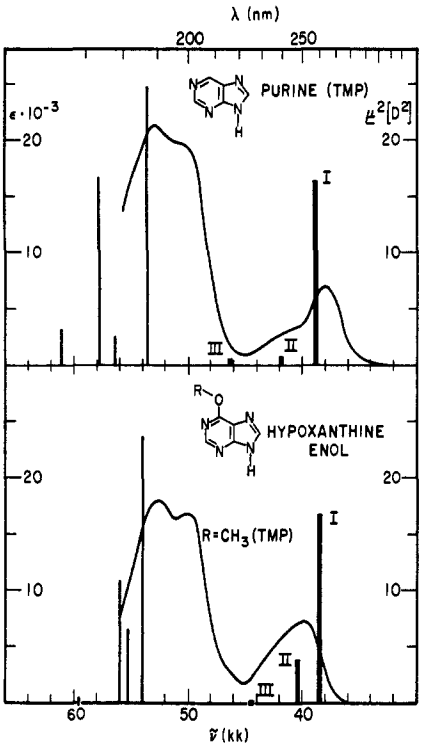


Figure 10. The spectrum of purine in TMP (above) and 6-methoxypurine in TMP (below) with the calculated in-plane transitions of purine and the enol of hypoxanthine.

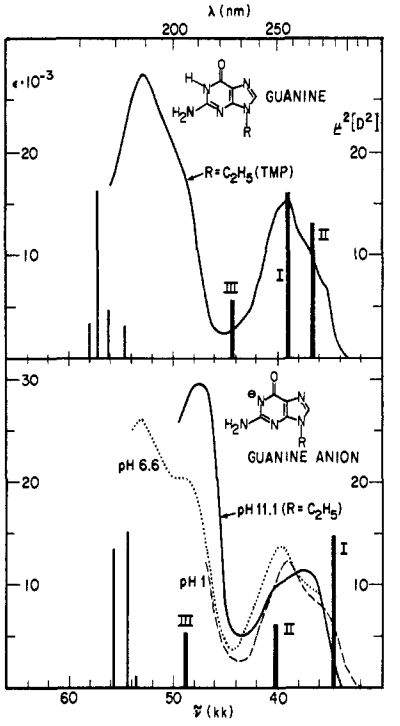


Figure 11. The spectrum of 9-ethylguanine in TMP with the calculated in-plane transitions (above), and the spectra of 9-ethylguanine at pH 6.6 and 11.1 (below) with the calculated in-plane transitions of the anion.

The calculated differences are, however, similar to those found for the keto forms of guanine and hypoxanthine and will therefore be discussed below.

The *anion of guanine* has an A-type spectrum like the enol rather than the H-type one of guanine in the keto form. The energy shifts of the transitions I, II, and III relative to their positions in the keto form are more pronounced for the anion than for the enol. The intensity of transition II is higher than usual for A-type spectra though still lower than that of I. The calculated spectrum of the anion and the spectrum observed for 9-ethylguanine at pH 11.1 (Figure 11) are in good agreement with regard to energies as well as relative intensities (I: exptl, 37 kK, calcd, 35 kK; II: exptl, 40 kK, calcd, 40 kK).

Bases *protonated at the five ring* constitute the last group to be discussed in this section. Compared to nonprotonated species, transition II always appears raised in energy and transition I lowered. Neutral bases with H-type spectra therefore show A-type spectra upon protonation at N7. In Figure 8 the calculated spectra of the two tautomers of *guanine* with the hydrogen atoms at N1 and N3, respectively, both protonated at N7, are depicted. The two spectra are very similar except that the energy of I is slightly higher and that of II slightly lower in the N3 tautomer and the intensity of its spectrum lower. (These differences parallel those found for the neutral tautomers.) It is normally assumed that the structure of guanine at low pH values corresponds to the N1 tautomer protonated at N7.[49] Our calculated intensity distribution disagrees with the observed one for guanosine at pH 1 (Figure 11). However, the influence of the substituent present at N9 on the intensity of the spectrum is not known.

The spectra of neutral bases with A-type spectra suffer rather drastic changes when protonation occurs at N7. In *adenine* transition II is removed from the neighborhood of I and shifted even above III in energy. As found for guanine protonated at N7, the intensity of II is comparable with that of I. The calculated overall changes in the adenine spectrum are large enough to rule out the possibility that protonation occurs at N7 in solution.

Bases with Hypoxanthine-Type Spectra. H-Type spectra are calculated for all bases carrying a proton at a nitrogen atom of the six-membered ring, *i.e.*, all purine bases with a carbonyl or imino group in position 6 or bases protonated either at N1 or N3. Available experimental evidence agrees with our calculations.

The structure of the *imine of adenine* is closest to that of hypoxanthine. The calculated spectra of both molecules are virtually superimposable with transition II lowest and well separated from I (Figure 9). Structurally, the imine differs from the amine by the transfer of a proton from the amino group to one of the nitrogen atoms of the six ring. *Protonation of adenine* at the six ring, *i.e.*, attaching a proton at N1 or N3 without abstracting a proton of the amino group, should lead to a spectrum which is intermediate to those of the amino and imino tautomer. This is the case. The calculated spectrum is of the H type rather than the A type with transition II lower than I but too close to show up as an individual peak. The observed spectrum of adenine does not change much on protonation with regard to intensity and energy, but the alterations in shape nicely confirm our results (Figure 12). Crystal reflection spectra of adenine hydrochloride[47] show that the weaker transition in protonated adenine lies indeed at lower energy than the strong one. On the basis of uv spectra, no decision can be made between

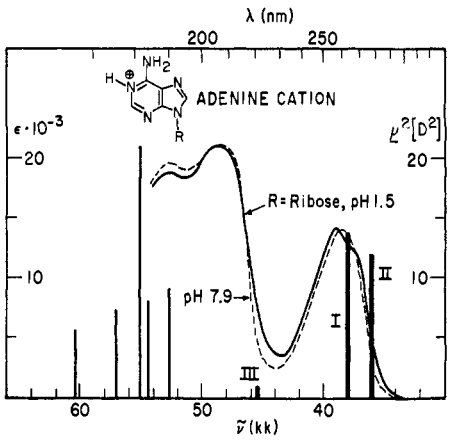


Figure 12. The spectrum of adenosine at pH 7.9 and 1.5 with the calculated in-plane transitions of adenine protonated at N1.

N1 and N3 as sites of protonation, as the calculated spectra for both tautomers are similar.

Guanine and *xanthine* differ from hypoxanthine by the presence of an amino and carbonyl group, respectively, in position 2. As found earlier for the enol of guanine, the presence of a substituent at C2 does *not* affect the type of spectrum but leads to an increase of the intensity of the transitions I, II, and III. At low energy the observed[50] and the calculated spectra of the diketo form of xanthine resemble closely those of guanine. Presumably, enolization of the carbonyl group in position 2 would therefore affect only the higher energy portion of the xanthine spectrum appreciably. In 9-ethylguanine (Figure 11), the stronger transition I is observed at 39 kK (255 nm) and the weaker II as a shoulder at 36 kK (275 nm). The calculated energies are 39 and 37 kK. The figures for xanthosine at pH 7 read[18] 42 kK (240 nm; calcd 40 kK) and 38.5 kK (260 nm; calcd 37 kK). For both molecules the calculated gap between the two transitions is slightly smaller than the observed one and they merge in the broadened spectra. The lower energy and higher intensity observed for guanine are calculated correctly. Transition III is calculated at 44 kK (225 nm) in guanine and probably corresponds to the flattening observed in the spectrum taken in trimethyl phosphate between 43 and 45 kK (230 to 220 nm) (Figure 11). In the diketo form of xanthine, III is shifted toward higher energy and should occur around 50 kK. For *guanine* and *hypoxanthine* we have investigated the changes to be expected if the *proton from N1 is transferred to N3* (Figure 9). They are rather small and consist mainly in a decrease of the sum of the intensities of transition I and II. This is similar to the differences found for adenine protonated at N3 instead of N1.

If we protonate *guanine at N3* we get a species which carries two protons at the six ring. Compared to a base like the enol of guanine with no protons at the six ring we see that the energy shifts for transition I and II correspond roughly to the sum of those caused by either a proton at N1 or N3. The intensity is intermediate between those found for the neutral N1 and N3 tautomers. The observed spectrum for guanine in aqueous solution of pH 1 is in good agreement with the calculated spectrum both with respect to the energies and relative intensities of the two lowest transitions. If we assume N7 as the site of protonation instead of N3, experimental and calculated spectra are in equally good agreement in energetic respects (exptl 36 kK (280 nm) and 39 kK (255 nm); calcd for both protonated species, 35 and 40 kK), but as pointed out earlier, the relative intensities of the two lowest transitions disagree. Yet, we do not consider the intensity difference significant enough to suggest N3 as the site of protonation in aqueous solution.

Appendix. The CNDO Parameters

The matrix elements F_{qs} of the Hartree–Fock matrix using a basis set of s and p atomic orbitals read in the CNDO approximation as follows.[33]

$$F_{qq} = U_{qq} + (P_{AA} - {}^1/_2P_{qq})\gamma_{AA} + \sum_{B\neq A}(P_{BB}\gamma_{AB} - V_{AB})$$

$$F_{qs} = \beta_{AB}S_{qs} - {}^1/_2P_{qs}\gamma_{AB}$$

P_{qs} are the elements of the population matrix and P_{AA} the total valence shell electron density associated with atom A. χ_q is assumed to belong to atom A and χ_s to atom B. With the overlap integral $S_{qs} = 0$ and the electron repulsion integral $\gamma_{AB} = \gamma_{AA}$, the last equation applies also to off-diagonal matrix elements with χ_q and χ_s both on atom A.

The one-center integrals U_{qq}, *i.e.*, the atomic core matrix elements, and the γ_{AA} are given in Table III.

Table III. The One-Center Parameters Used in Our Calculation[a]

	ζ	U_{ss}, eV	U_{pp}, eV	γ_{AA}, eV	β'_A, eV Å
H	1.200	−13.595		10.921	−17.278
C	1.625	−45.993	−36.937	8.676	−23.401
N	1.950	−63.461	−51.216	9.394	−28.079
O	2.275	−91.086	−74.064	11.581	−32.757

[a] ζ is the Slater exponent.

The values of U_{qq} were determined similar to those in ref 51, but the values of γ_{AA} used in the corresponding formulas are those used in the present calculation. To account for the in-plane and out-of-plane part of the complex spectra of nucleic acid bases, it proved necessary to lower the values of γ_{AA} by 15%. This is actually a minor alteration compared to the differences between γ_{AA} values currently in use.

The two-center integrals were chosen as follows. The electron-core potential integrals V_{AB} were set equal to $Z_B\gamma_{AB}$, where Z_B is the core charge of atom B. For the resonance integral β_{AB} we followed the proposition of Wratten[52] with a slight modification

$$\beta_{AB} = \frac{\beta'_A + \beta'_B}{2R_{AB}} K_{\sigma,\pi}$$

with $K_\pi = 0.68$ and $K_\sigma = \sqrt{K_\pi}$ (π and σ functions are defined in local coordinates).

For the γ_{AB} we used the formula of Kuhn[32]

$$\gamma_{AB} = \gamma_{AB}{}^{th} - \alpha \exp(-\eta R^n_{AB})$$

with $\eta = 0.71$ Å^{-n}, $n = 1.80$. $\gamma_{AB}{}^{th}$ is the analytical

(50) G. H. Beaven, E. R. Holiday, and E. A. Johnson in "The Nucleic Acids," Vol. I, E. Chargaff and J. N. Davidson, Ed., Academic Press, New York, N. Y., 1955, p 512.

(51) J. M. Sichel and M. A. Whitehead, *Theor. Chim. Acta*, 7, 32 (1967).

(52) R. J. Wratten, *Chem. Phys. Lett.*, 1, 667 (1968).

integral $(S_A(1)S_A(1)|S_B(2)S_B(2))$ and α is the difference between $\gamma_{AB}{}^{th}$ and the γ_{AA} values tabulated in Table III. If A and B are different types of atoms, the arithmetic mean is used.

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Electronic Structure of Small Organic Free Radicals[1a]

James M. Howell*[1b] and Poul Jørgensen[1c]

Contribution from the Quantum Theory Project, University of Florida, Gainesville, Florida 32601. *Received August 8, 1972*

Abstract: The effects of geometry change and substitution on the electronic structure of some small free radicals are examined using a modified INDO/CI formalism. The nature of the lowest excitation is found to change from being SOMO (singly occupied molecular orbital) → LUMO (lowest unoccupied molecular orbital), for a planar radical site, to HDOMO (highest doubly occupied molecular orbital) → SOMO, for a pyramidal radical site. The effects of π donors and acceptors are evaluated and found to be comparable to the effect of geometry. Geometrical preferences are investigated for the model structures. Planar radical sites are preferred.

The electronic structure of small organic radicals has been a subject of continuing interest. While most of the work has been concerned with the calculation of spin properties,[2] there has been effort toward the calculation of ionization potentials[3] and geometry[2b,4] as well as electronic spectra.[5] In this paper we present some simple calculations on radicals, both charged and neutral, which may serve as model structures for large classes of organic radicals.

Method

The molecular orbitals were calculated by the INDO[6] method. The INDO method has been frequently used to investigate free radicals.[7] The used parameterization was essentially the same as that developed by Jaffé and Del Bene for spectral CNDO investigations of planar systems.[8] However, because we wanted a method which would handle nonplanar structures we modified their approach to π orbitals.

Jaffe and Del Bene[8] decreased the β matrix elements between orbitals that were perpendicular to the molecular plane (the π orbitals) by a factor K

$$\beta^{\pi}_{ij} = (\beta^0_i + \beta^0_j)K(S_{ij}/2) \quad (1)$$

Instead, we divide the overlap, S_{ij}, between each pair of atomic orbitals into a σ (S^{σ}_{ij}) component and a π component (S^{π}_{ij}) within a local framework determined by the internuclear axis. The π part is then decremented (eq 2) and the β matrix element calculated on the basis of the adjusted overlap S'_{ij} (eq 3).

$$S_{ij} = S^{\sigma}_{ij} + S^{\pi}_{ij}$$

$$S'_{ij} = S^{\sigma}_{ij} + KS^{\pi}_{ij} \quad (2)$$

$$\beta_{ij} = (\beta^0_i + \beta^0_j)(S'_{ij}/2) \quad (3)$$

A value of 0.65 for K was found to yield good spectral energies for a variety of closed shell systems and was used in our calculations. The grand canonical Hartree–Fock approximation[9,10] was employed for the calculation of the molecular orbitals and total energies for the radical species. In this method, the unpaired electron in spatial orbital i is assumed, on the average, to be equally distributed between $i\alpha$, the spin up MO, and $i\beta$, the spin down MO, each thus having an occupancy of $^1/_2$ electron. Formally similar approaches have been used before for free radicals[10] and transition metals.[9] Additionally, Slater has used fractional occupation numbers in the Hyper-Hartree-Fock method.[11]

The CI calculation necessary to obtain the excitation spectrum was carried out in a fashion consistent with

(1) (a) This work was supported in part by the Air Force Office of Scientific Research through Grant AFOSR-71-1714B, and in part by the National Science Foundation through Grant NSF-GP-16666; (b) author to whom correspondence should be addressed at Department of Chemistry, Vanderbilt University, Nashville, Tenn.; (c) Department of Chemistry, University of Aarhus, Aarhus, Denmark.

(2) (a) S. Y. Chang, E. R. Davidson, and G. Vincow, *J. Chem. Phys.*, **52**, 1740 (1970); A. T. Amos and B. L. Burrows, *ibid.*, **52**, 3072 (1970); P. Carsky and R. Zahradnik, *J. Phys. Chem.*, **74**, 1240, 1249 (1970); J. Baudet and M. Suard, *J. Chim. Phys. Physiochim. Biol.*, **67**, 1088 (1970); V. A. Kuprievich, Y. A. Kruglyak, and E. V. Mozdor, *Int. J. Quantum Chem.*, **4**, 73 (1970); L. Pauling and G. W. Wheland, *J. Chem. Phys.*, **1**, 362 (1933); H. Konishi and K. Morokuma, *J. Amer. Chem. Soc.*, **94**, 5603 (1972); (b) S. Y. Chang, E. R. Davidson, and G. Vincow, *J. Chem. Phys.*, **52**, 5596 (1970).

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