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CNDO and INDO Calculations of the Magnetic Circular Dichroism of Several Purine Derivatives

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Calculations of the magnetic circular dichroism(MCD) of methylpurines and methyladenines were carried out not only by the CNDO/S-CI procedure, but also by the INDO/S-CI procedure. The CNDO/S-CI procedure correctly predicted the signs and magnitudes of the MCD spectra of 1-, 3-, and 7-methylpurines and of 9-methyladenine which cannot be improved by the parameter adjustment. On the other hand, the signs of the MCD spectra and transition energies of all these purine derivatives were clearly explained by the INDO/S-CI procedure.

The magnetic circular dichroism (MCD) spectra of purine derivatives have been extensively studied by many investigators because the MCD spectra give valuable information on the electronic structure of these compounds.[1–3] By MCD the electronic absorption bands which overlap with each other have been resolved, and the presence of several electronic transitions in the ultraviolet region has been clarified.

On the other hand, there have been many attempts to calculate the Faraday parameters of the organic aromatic compounds by means of quantum mechanical SCF-MO calculations. The Pariser-Parr-Pople(PPP) procedure[4] has been successfully applied to explaining the signs of the MCD spectra of the derivatives and hetero atom analogues of alternant and nonalternant aromatic hydrocarbons.[5] The complete neglect of the differential overlap (CNDO) method,[6,7] an SCF-MO procedure for all valence electrons, has also predicted the correct signs of the MCD spectra of indole,[8] azines,[9] substituted benzenes,[10,11] some alternant hydrocarbons,[12] and azanaphthalenes.[13]

However, the original CNDO/S-CI procedure[7] proposed by Jaffé and his co-workers has failed to reproduce the MCD spectra of methyladenines and some 8-azapurines.[3] In order to overcome the difficulty, Djerassi and his co-workers have set the scaling constant, κ, for the π-type overlap integrals back to unity, as in the CNDO/2 method, and scaled the state energies and all the quantities derived from energies by means of an adjustable parameter, κ', after the CI calculation had been performed.[3] Although the new method, labeled the CNDO/S' method, has correctly predicted the signs of the MCD spectra of methyladenines and 8-azapurines, it cannot give wavefunctions which take account of the transition energies as well as the sign of the MCD spectra.

In this work, we calculate the transition energies and the Faraday *B* terms of purine, methylpurines, and methyl adenines not only by means of the CNDO procedure, but also by means of the intermediate neglect of the differential overlap(INDO) approximation,[14,15] and compare the results with the experimental data which have appeared in the literature.

Theoretical

The Faraday *B* terms were calculated using wavefunctions obtained from the INDO/S-CI approximation. The one-center core integrals and one-center electron repulsion integrals were evaluated from the valuence-state energy data[16] and the experimental Slater-Condon parameters.[17] The two-center electron repulsion integrals were calculated by means of the Nishimoto-Mataga equation.[18] The resonance integrals, $\beta_{\mu\nu}$, between atomic orbitals, μ and ν, were evaluated by means of the following equation:

$$\beta_{\mu\nu} = \frac{1}{2}(\beta_{\mathrm{A}}+\beta_{\mathrm{B}})\bar{S}_{\mu\nu}, \tag{1}$$

where β_{A} is a bonding parameter of the atom, A, to which the atomic orbital, μ, belongs and where $\bar{S}_{\mu\nu}$ is an overlap integral obtained as follows:

$$\bar{S}^{\mathrm{ss}}_{\mu\nu} = S^{\mathrm{ss}}_{\mu\nu}, \tag{2}$$

$$\bar{S}^{\mathrm{sp}}_{\mu\nu} = S^{\mathrm{sp}}_{\mu\nu} \tag{3}$$

$$\bar{S}^{\mathrm{pp}}_{\mu\nu} = S^{\sigma\sigma}_{\mu\nu}g^{\sigma\sigma}_{\mu\nu}\kappa_{\sigma\sigma} + S^{\pi\pi}_{\mu\nu}g^{\pi\pi}_{\mu\nu}\kappa_{\pi\pi}, \tag{4}$$

where $g^{\sigma\sigma}_{\mu\nu}$ and $g^{\pi\pi}_{\mu\nu}$ are the geometric factors and where $\kappa_{\sigma\sigma}$ and $\kappa_{\pi\pi}$ are the semiempirical scaling factors. The bonding parameters, β, and the scaling factors are determined so that the ionization potentials and transition energies of benzene and pyridine are well reproduced ($\beta_{\mathrm{H}}=-6.6$ eV, $\beta_{\mathrm{C}}=-15.4$ eV, $\beta_{\mathrm{N}}=-23$ eV, $\kappa_{\sigma\sigma}=1.23$, $\kappa_{\pi\pi}=0.67$). The configuration interaction(CI) among singly excited configurations below 10 eV was taken into account.

We also calculated the Faraday *B* terms of the purine derivatives within the framework of the CNDO/S-CI approximation. The one-center repulsion integrals and one-center core parameters were taken from the values determined by Sichel and Whitehead.[19] The two-center electron integrals were evaluated by the Nishimoto-Mataga equation.[18] The bonding parameter, β, and the scaling factor for the π-type overlap integrals, κ, were empirically chosen in the same way as the INDO/S calculation ($\beta_{\mathrm{H}}=-6.6$ eV, $\beta_{\mathrm{C}}=-17.8$ eV, $\beta_{\mathrm{N}}=-28$ eV, $\kappa_{\sigma\sigma}=1.0$, $\kappa_{\pi\pi}=0.59$).

The molecular structures of 7*H*-purine[20] and 9-methyladenine[21] have been clarified by X-ray crystal analysis. However, no experimental data for the structures of the remaining compounds have been reported. The bond lengths and the bond angles of the 7*H*-purine ring of 7-methylpurine and 7-methyladenine were taken from those of 7*H*-purine. The molecular structure of the 9*H*-purine ring of 9-methylpurine was set equal to those of 9-methyladenine. The geometries of 1- and 3-methylpurines were assumed to be the combinations of the geometry of the tautomeric forms of isocytosine[22] for the pyrimi-

Table 1. Experimental and theoretical results for purine and methylpurines

Compd	Exptl[a]		Calcd (INDO/S)		Calcd (CNDO/S)		
	$\tilde{\nu}\times10^{-3}$ cm^{-1}	$B\times10^4$ βD^2 cm	$\tilde{\nu}\times10^{-3}$ cm^{-1}	$B\times10^4$ βD^2 cm	$\tilde{\nu}\times10^{-3}$ cm^{-1}	$B\times10^4$ βD^2 cm	
Purine			30.7	−2.4	33.0	−1.4	A″
			35.2	−0.4	37.5	0.2	A″
	37.9	−8.7	36.7	−10.6	37.2	−7.6	A′
			40.0	0.2	41.2	−0.7	A″
	41.2	16.8	42.0	25.0	43.0	15.0	A′
			43.3	−0.7	44.2	−0.3	A″
1-Methylpurine			27.9	−0.3	30.3	0.2	A″
			29.8	−0.6	31.5	0.0	A″
	33.9	−	30.8	−9.0	32.5	−13.9	A′
			32.3	0.7	36.5	3.6	A″
	35—37	+	35.4	11.8	35.9	16.6	A′
			38.5	−23.2	42.0	1.4	A″
	41—43	−	39.2	17.2	41.0	−12.1	A′
			43.7	−2.9	45.0	−0.5	A′
3-Methylpurine			29.0	−0.4	31.6	0.1	A″
	33.6	−	30.7	−18.8	32.9	−48.5	A′
	36—39	+	34.2	59.9	34.2	67.8	A′
			34.4	−20.0	36.8	−0.1	A″
			36.3	−8.1	37.5	−5.7	A″
			40.9	−0.4	42.2	−0.4	A″
	42—	−	42.2	−39.9	42.5	−26.8	A′
7-Methylpurine			30.7	−2.4	33.1	−1.5	A″
			35.2	−0.3	37.5	−0.2	A″
	37.3	−	36.4	−14.5	39.1	−9.8	A′
			39.7	−2.9	41.4	−1.4	A″
	40—43	+	40.7	32.6	42.2	22.8	A′
			43.4	−0.4	44.2	−0.1	A″
			45.4	−0.9			A″
	47—	−	46.5	−58.9	47.1	−25.9	A′
			47.4	56.3	49.4	55.9	A′
9-Methylpurine			30.9	−2.3	33.5	−1.2	A″
			34.9	−0.1	36.7	0.2	A″
	37.1	−	37.0	−2.6	37.7	8.4	A′
	40—42	+	40.7	6.8	41.5	−12.3	A′
			41.0	−2.4	42.0	−5.8	A″
			43.0	0.6	44.7	0.0	A″
	47—	−	46.1	−11.3	47.2	6.1	A′

a) The experimental data of the methylpurines are taken from Ref. 2.

dine ring with that of 7*H*-purine for the imidazole ring. The bond lengths and bond angles of the methyl and amino groups were assumed to be the same as those of 9-methyladenine.

The Faraday *B* term of a transition from the ground state, *a*, to the excited state, *j*, is given by:[23]

$$B_{j\leftarrow a} = \sum_{k\neq a,j} B_{j,k} + \sum_{k\neq a,j} B_{k,a} + B_{j,a} \tag{5}$$

$$B_{j,k} = \mathrm{Im}\langle j|\boldsymbol{\mu}|k\rangle\cdot\langle a|\boldsymbol{m}|j\rangle \times \langle k|\boldsymbol{m}|a\rangle/(E_k-E_j) \tag{6}$$

$$B_{k,a} = \mathrm{Im}\langle k|\boldsymbol{\mu}|a\rangle\cdot\langle a|\boldsymbol{m}|j\rangle \times \langle j|\boldsymbol{m}|k\rangle/(E_k-E_a) \tag{7}$$

$$B_{j,a} = \mathrm{Im}\langle j|\boldsymbol{\mu}|a\rangle\cdot\langle a|\boldsymbol{m}|j\rangle \times (\langle j|\boldsymbol{m}|j\rangle-\langle a|\boldsymbol{m}|a\rangle)/(E_j-E_a) \tag{8}$$

In Eqs. 6—8, $\boldsymbol{m}$ and $\boldsymbol{\mu}$ are the electric and magnetic moment operators respectively, and E_a, E_j, and E_k are energies of the *a*, *j*, and *k* states respectively. $B_{j,k}$ stands for the magnetic mixing of the *k* state with the excited state, *j*, and $B_{k,a}$ represents the coupling of the *k* state to the ground state, *a*. $B_{j,a}$ arises from the magnetic mixing between the ground state, *a*, and the excited state, *j*.

The electric transition moments were evaluated by the dipole length method. The LCAO-MO coefficients regarding the orthogonalized INDO atomic orbital basis were deorthogonalized by the inverse Löwdin transformation[24], and the atomic integrals

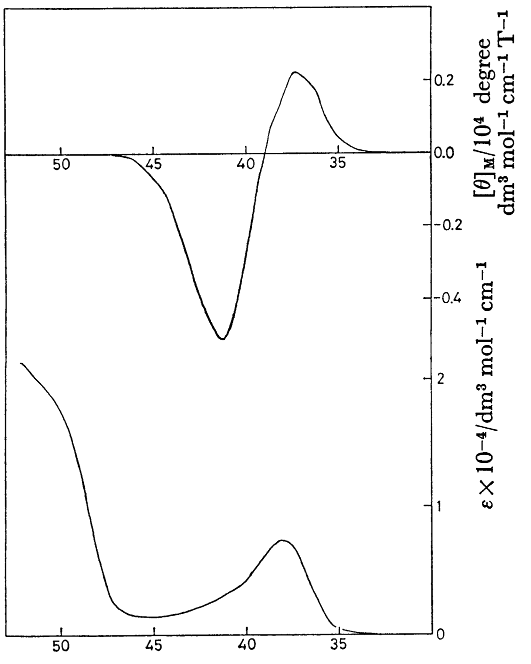

Fig. 1. MCD (upper) and absorption (lower) spectra of purine in aqueous solution (pH 7) at room temperature.

were calculated using Slater atomic orbitals,[25] in accordance with the description of Refs. 26 and 27.

The Faraday *B* terms calculated for non-centric molecules using a limited basis set are origin-dependent.[28,29] In this work, the origin was placed at the center of the electron cloud in the molecule, according to the theoretical argument of Caldwell and Eyring.[29]

Computations were carried out using an ACOS 700 computer in the computer center of Tohoku University.

Results and Discussion

The MCD and absorption spectra of purine are presented in Fig. 1. The molar ellipticity $[\theta]_M$ per unit of magnetic field is shown in degree $dm^3\ mol^{-1}\ cm^{-1}\ T^{-1}$. The intense absorption band observed at 38100 cm^{-1} is resolved into two in the MCD spectrum. The positive MCD band is assigned to the lowest $\pi^*\leftarrow\pi$ transition, and the negative one, to the second $\pi^*\leftarrow\pi$ transition.

The results calculated for purine and methylpurines are given in Table 1, along with the experimental data. The experimental values of the Faraday *B* terms of purine were obtained by a gaussian curve-fitting procedure. The experimental data for methylpurines were taken from the spectra reported by Townsend *et al.*[2] The sign pattern of the MCD of methylpurines is the same as that of purin itself. The transition energies of 7-methylpurine and 9-methylpurine are close to those of purine, whereas the MCD bands of 1-methylpurine and 3-methylpurine are shifted to a lower wavenumber region relative to purine. For purine, 1-methylpurine, 3-methylpurine, and 7-methylpurine, both INDO/S-CI and CNDO/S-CI procedures correctly predict the sign of the MCD spectra and the band positions of these compounds. On the other hand, a remarkable difference between the INDO/S-CI result and the CNDO/S-CI result is found for 9-methylpurine. Although the INDO/S-CI procedure explains the sign of the MCD of 9-methylpurine well, the sign of the MCD of 9-methylpurine calculated by the CNDO/S-CI procedure is the opposite of that of the experiments.

In the lowest wavenumber region, two $\pi^*\leftarrow n$ transitions with A″ symmetry are predicted. In the MCD and absorption spectra, $\pi^*\leftarrow n$ transitions are hidden behind the stronger $\pi^*\leftarrow\pi$ transitions, and none of them is observed separately. However, 7-ribosyl purine exhibits a negative CD band, at 35200 cm^{-1}, which arises from the $\pi^*\leftarrow n$ transition.[30] A weak out-of-plane polarized band was observed at 34000 cm^{-1} in the polarized absorption spectrum of the crystal of 7-methylpurine and assigned to the $\pi^*\leftarrow n$ transition.[31] The calculated transition energy of the lowest $\pi^*\leftarrow n$ transition agrees fairly well with these experimental findings.

The magnitudes of the calculated Faraday *B* terms of the $\pi^*\leftarrow n$ transitions are smaller than those of the $\pi^*\leftarrow\pi$ transitions, except for the fourth $\pi^*\leftarrow n$ transition of 1-methylpurine and the second $\pi^*\leftarrow n$ transition of 3-methylpurine. The relatively large *B* terms of the $\pi^*\leftarrow n$ transitions of 1- and 3-methylpurines are interpreted as mainly arising from the magnetic coupling of the neighbouring $\pi^*\leftarrow\pi$ state with the $\pi^*\leftarrow n$ state.

The experimental and theoretical results for methyladenines are shown in Table 2. The experimental transition energies and Faraday *B* terms are taken from Ref. 3. The substitution of the amino group on the purine ring reverses the sign of the MCD spectra and causes a slight red shift. The INDO/S-CI procedure takes good account of the sign of the MCD spectra of these methyladenines, except for the lowest $\pi^*\leftarrow\pi$ transition of 7-methyladenine. The CNDO/S-CI method cannot reproduce the sign of three lowest MCD bands of 7-methyladenine.

The effects of the bonding parameter of the nitrogen atom, β_N, on the *B* terms calculated by the INDO/S-CI procedure are given in Table 3. In the INDO/S-CI calculation, the signs of the Faraday *B* term of 7-methyladenine are sensitive to the bonding parameter of the nitrogen atom, β_N. The unsatisfactory results for the sign of the lowest MCD band of 7-methyladenine are improved by increasing the value of $|\beta_N|$. We have also calculated the *B* terms of 7-methyladenine and 9-methylpurine by the CNDO/S-CI method with $\beta_N=-20$ eV and -35 eV. However, the calculated signs of the *B* terms of these compounds were not improved.

Recently Michl has shown that the sign of the Faraday *B* term of $\pi^*\leftarrow\pi$ transitions in cyclic π-systems with $(4N+2)\pi$ electrons can be predicted by a simple rule.[5] The sign of the *B* term of the lowest $\pi^*\leftarrow\pi$ transition is the same sign as the difference in the energy gap of the two lowest unoccupied molecular orbitals (ΔLUMO) from that of the two highest occupied molecular orbitals (ΔHOMO), (ΔHOMO—

TABLE 2. EXPERIMENTAL AND THEORETICAL RESULTS FOR METHYLADENINES

Compd	Exptl$^{a)}$		Calcd (INDO/S)		Calcd (CNDO/S)		
	$\tilde{\nu}\times10^{-3}$	$B\times10^{4}$	$\tilde{\nu}\times10^{-3}$	$B\times10^{4}$	$\tilde{\nu}\times10^{-3}$	$B\times10^{4}$	
	cm^{-1}	βD^{2} cm	cm^{-1}	βD^{2} cm	cm^{-1}	βD^{2} cm	
7-Methyladenine			33.4	−1.3	35.8	−0.2	A″
	36.2	2.6	35.1	−1.2	36.1	−4.8	A′
			35.4	0.0	38.3	−0.6	A″
	38.6	−4.0	39.9	−9.4	41.6	0.3	A′
			40.4	4.9	41.9	7.8	A″
			41.1	0.2	45.2	0.0	A″
	41.8	4.5	43.9	11.1	45.8	−30.5	A′
			44.3	1.3			A″
	45.5	14.7	45.8	42.7	46.6	61.8	A′
			46.8	−0.6			A″
	49.0	−6.2	47.1	−60.0	49.6	−38.6	A′
9-Methyladenine			34.0	−0.2	36.8	0.0	A″
			35.5	−1.1	37.4	−12.2	A″
	36.6	8.6	36.2	33.0	37.4	57.4	A′
	39.2	−7.4	38.2	−45.8	39.2	−59.0	A′
			41.8	−1.1	42.1	−1.3	A″
			43.8	0.1	45.7	−0.1	A″
			44.3	0.7			A″
	42.9	0.8	44.9	11.1	45.7	8.5	A′
			45.5	7.6			A″
	46.2	17.8	47.1	37.1	49.5	53.3	A′
			47.5	−9.5	50.2	−6.2	A″
	49.5	−15.0	48.7	−47.3	51.5	−43.3	A′

a) Ref. 3.

TABLE 3. DEPENDENCE OF THE FARADAY B TERMS CALCULATED BY THE INDO/S PROCEDURE ON THE BONDING PARAMETER OF THE NITROGEN ATOM, β_{N}

Compd		Calcd ($\beta_{N}=-23$ eV)		Calcd ($\beta_{N}=-25$ eV)		Calcd ($\beta_{N}=-27$ eV)		Exptl$^{a)}$
		$\tilde{\nu}\times10^{-3}$	$B\times10^{4}$	$\tilde{\nu}\times10^{-3}$	$B\times10^{4}$	$\tilde{\nu}\times10^{-3}$	$B\times10^{4}$	$B\times10^{4}$
		cm^{-1}	βD^{2} cm	cm^{-1}	βD^{2} cm	cm^{-1}	βD^{2} cm	βD^{2} cm
7-Methyladenine	A″	33.4	−1.3	33.7	−1.1	34.1	−0.9	
	A′	35.1	−1.2	36.1	3.7	36.9	7.7	2.6
	A″	35.4	0.0	35.9	−1.4	36.3	−0.9	
	A′	39.9	−9.4	40.7	−13.9	41.2	−19.0	−4.0
	A″	40.4	4.9	41.3	0.7	41.9	−2.6	
	A″	41.1	0.2	43.5	0.1	45.0	1.1	
	A′	43.9	11.1	45.1	14.7	46.3	20.1	4.5
	A″	44.3	1.3	44.7	2.1	45.3	1.0	
	A′	45.8	42.7	47.4	54.2	48.5	67.8	14.7
	A″	46.8	−0.6	48.3	10.5	48.1	−11.6	
	A′	47.1	−60.0	48.5	−88.0	49.8	−70.2	−6.2

a) Ref. 3.

ΔLUMO). Although the purine derivatives may deviate somewhat from the weakly perturbed 10 electron annulenes, it is a fact that the energy of the frontier molecular orbitals is an important factor in determining the sign of the MCD spectra. The values of (ΔHOMO−ΔLUMO) calculated by the INDO/S-CI method are negative or almost zero for methylpurines and positive for methyladenines. However, the CNDO/S-CI method predicts a large positive value for the difference, (ΔHOMO−ΔLUMO), of 9-methylpurine, leading to the positive B value for the lowest $\pi^{*}\leftarrow\pi$ transition.

The two LUMO's and the two HOMO's of 9-methylpurine obtained from the INDO/S calculation are shown in Fig. 2. The LCAO-MO coefficients obtained by the CNDO/S method are analogous to

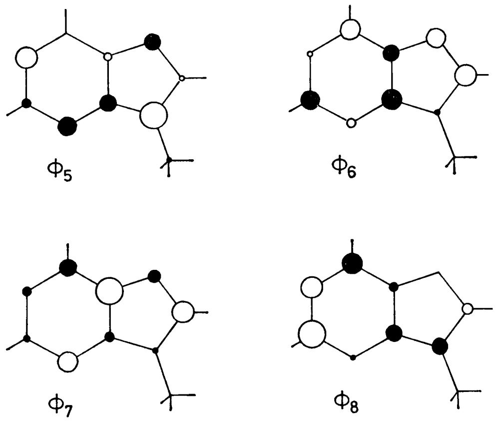

Fig. 2. LCAO-MO coefficients of the highest occupied π molecular orbitals, ϕ_5 and ϕ_6, and the lowest unoccupied π molecular orbitals, ϕ_7 and ϕ_8 of 9-methylpurine. White and black circles represent positive and negative signs, respectively.

those obtained by the INDO/S method and so are not shown here. The orbital energies of the HOMO, ϕ_6, and the LUMO's, ϕ_7 and ϕ_8, calculated by the CNDO/S method are almost the same as those calculated by the INDO/S method, whereas the CNDO/S method predicts the energy of the molecular orbital, ϕ_5, to be lower by 0.53 eV than that calculated by the INDO/S method. This is because the CNDO/S method does not discriminate the energy of one π-electron in the pyrrole-type nitrogen atom having two π-electrons from that in the pyridine-type nitrogen atom with one π-electron, and gives poor results for the energy of the molecular orbital, ϕ_5, in which the LCAO-MO coefficients of the nitrogen atoms are larger than in other molecular orbitals; although the semi-empirical valence-state ionization potentials, $I_p\{N(SP^2PP)\rightarrow N(SPPP)\}$ and $I_p\{N(SP^2PP)\rightarrow N(SP^2P)\}$, are 12.48 eV and 14.42 eV respectively,[16] the CNDO/S method does not distinguish between them.

The INDO/S-CI procedure is superior to the CNDO/S-CI procedure in that the former can discriminate the ionization potential of the pyrrole-type nitrogen atom from that of the pyridine-type nitrogen atom, and predicts correct signs of the Faraday B terms of 9-methylpurine and 7-methyladenine.

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