Near-Ultraviolet Vibronic Transitions of Adenosine 5′-Phosphate, Adenosine, and Its Complexes with *cis*- and *trans*-Diamminedichloroplatinum(II): Spectral Study of Isotropic Absorption, Linear Dichroism, and Circular Dichroism

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Abstract: The solution isotropic absorption, circular dichroic, and stretched film dichroism spectra of adenosine, its complexes with *cis*- and *trans*-diamminedichloroplatinum(II), and AMP have been interpreted above about 250 nm in terms of two relatively close vibronic (π^*,π) transitions. This analysis leads to a self-consistent interpretation of the spectral activity of adenosine nucleosides observed in this region.

There is controversy over the number of electronic transitions, their positions and intensities, that contribute to the near-ultraviolet absorption spectrum, the so-called X band, of adenine nucleosides. Mason[1] inferred the existence of two in-plane polarized (π^*,π) transitions in the X band of the adenine moiety; these were later related to the spectrum of benzene and named B_{1u} and B_{2u}.[2,3] The presence of two (π^*,π) transitions in the X-band region was also supported by SCFMO-CI calculations;[4,5] however, no general agreement has been reached concerning their positions and relative intensities.[6-14] More recently, all-valence-electron CNDO/2 molecular orbital calculations[15] resulted in the suggestion of a third (π^*,π) transition near the blue tail of the X band. As a further complication, there is evidence for the presence of (π^*,n) transitions in the X band,[6,11,16] and although these play no detectable roles in isotropic absorption or emission spectra,[9] it has been conjectured that at least one (π^*,n) transition contributes significantly to the CD spectrum of adenosine[14,17] in the X region. More recently published results[18-20] have not been able to resolve the above difficulties.

The work to be reported in this paper is a comparative study involving the detn. of three types of spectra of adenosine and three of its derivatives: adenosine 5′-phosphate (AMP) and 1:1 complexes of adenosine with both the cis and trans isomers of diamminedichloroplatinum(II). The spectra determined were those of the isotropic absorption and circular dichroism in neutral aqueous solutions and the linear dichroism of adenosine and its derivatives incorporated into stretched films of polyvinyl alcohol. Taking account of the *vibronic* nature of the transitions, the results lead to the unequivocal conclusion that the absorption, CD, and MCD spectra of adenine nucleosides at wavelengths greater than about 250 nm may be interpreted in terms of two (π^*,π) transitions alone.

Experimental Section

Adenosine and adenosine 5′-phosphate (AMP) were purchased from Sigma Chemical Co. (Lots 42C-2930 and 57C-7150, respectively) and used without further purification. Solutions of these materials were prepared in cacodylate buffer at pH 6.9. The diamminedichloro complexes were prepared by standard methods and recrystallized from hydrochloric acid.[21,22] Complexes with adenosine in 0.01 mol dm^{-3} sodium perchlorate were prepared as described previously.[23] We note that under the conditions used, the quantities of other than 1:1 complexes were completely negligible.[24]

Absorption spectra of solutions were determined by the use of a Zeiss DMR10 double beam recording spectrophotometer controlled by an INTEL 8080 microprocessor allowing the collection of data in user-specified steps (minimum 0.1 nm) for the desired number of scans followed by signal averaging. Linear dichroism was measured with a manual Zeiss PMQ II single beam spectrophotometer using an attachment designed to eliminate the need for scattering corrections.[25] The preparation of the stretched films of poly(vinyl alcohol) incorporating various solutes has been described before.[26] Films were stretched in general 4.5-fold.

A JASCO model 40CS spectropolarimeter was used to measure the circular dichroism of the solutions. The instrument was calibrated with *d*-10-camphorsulfonic acid and solution concentrations were selected to obtain optimum signal to noise ratios. The spectropolarimeter was equipped with a microprocessor, based on INTEL 8085, assembled and expanded by Mr. A. G. Snigg to the specification of Dr. M. Dwyer and Mr. G. E. Boehm who jointly did the programming. The microprocessor controls the operation of the spectropolarimeter, and among the facilities included, and of particular relevance to this work, is the accumulation of user-specified number of points (in multiples of 2^8 with 20 μs per point) in 32-bit precision followed by signal averaging. Details of this microprocessor will be published elsewhere.

Data reduction and curve-fitting procedures were done on a CDC Cyber 173 computer.

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Table I. Results of Fitting Spectra to Two Vibronic Progressions[a]

	adenosine	AMP	cis Pt	trans Pt
$\tilde{\nu}_{00}^{(1)}$	36400 (100)	36400 (100)	35300 (100)	35470 (90)
$\tilde{\nu}_{00}^{(2)}$	37100 (60)	37100 (50)	36900 (80)	36460 (100)
$X^{(1)}$	1.50 (0.07)	1.50 (0.07)	1.76 (0.08)	1.78 (0.30)
$X^{(2)}$	1.48 (0.05)	1.48 (0.04)	1.67 (0.04)	1.90 (0.06)
$(b_g)_{abs}$	2260 (65)	2260 (50)	2270 (200)	2260 (200)
$(b_g)_{CD}$	1670 (110)	1670 (100)	1720 (200)	1570 (140)
$f^{(1)}$			0.052	0.075
$f^{(2)}$	0.292	0.305	0.140	0.126
$-R^{(1)} \times 10^{40}$	1.97-2.27	0.33	2.02-2.07	1.27
$-R^{(2)} \times 10^{40}$	0-0.30	3.18	0-0.05	1.31

[a] Figures in brackets are linear estimates of the standard deviations of the best-fit parameters.

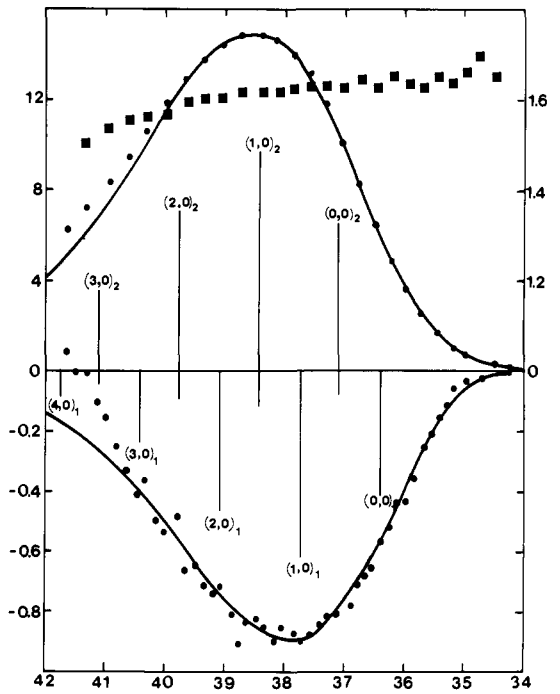

Figure 1. Spectra of adenosine. Squares, dichroic ratios in poly(vinyl alcohol) films stretched 4.5-fold; full lines, fitted isotropic absorption and circular dichroic spectra of solution, the vertical lines are proportional to the intensities of the individual vibronic bands and the lower and higher energy bands are distinguished by the subscripts 1 and 2, respectively; circles, experimental data. Ordinate: top lhs, $10^{-3}\epsilon$ (dm^3 mol^{-1} cm^{-1}); top rhs, dichroic ratio; bottom lhs, $\Delta\epsilon$ (dm^3 mol^{-1} cm^{-1}). Abscissa: $10^{-3}\tilde{\nu}$ (cm^{-1}).

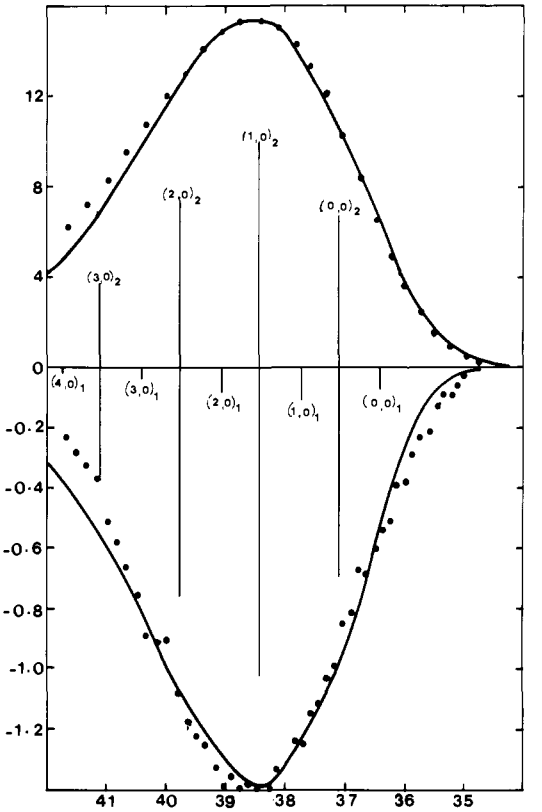

Figure 2. Spectra of AMP; symbols as in Figure 1. Ordinate: top lhs, $10^{-3}\epsilon$ (dm^3 mol^{-1} cm^{-1}); bottom lhs, $\Delta\epsilon$ (dm^3 mol^{-1} cm^{-1}). Abscissa: $10^{-3}\tilde{\nu}$ (cm^{-1}).

Results

In Figure 1 the dots represent the experimental absorption and CD spectra of adenosine; the square symbols correspond to the measured dichroic ratios in stretched films defined as the ratio of absorbances with light polarized parallel to and perpendicular with respect to the direction of stretch. The absorption and CD spectra are very nearly of identical shape, but the CD spectrum is shifted by about 700 cm^{-1} to the red compared with the absorption spectrum. This fact led to the assumption that, in the first approximation, the two spectra are due to two separate vibronic transitions, and we wrote each transition as an harmonic progression of Gaussian bands as described before.[27,28] Thus, as the first approximation, the absorptivity or circular dichroism, $I(\tilde{\nu})$, at a wavenumber $\tilde{\nu}$, is expressed as the sum

$$I(\tilde{\nu}) = \sum_{m=0} (I_{00}X^m/m!) \exp[-4 \ln 2\{b_g^{-2}(\tilde{\nu} - \tilde{\nu}_{00} - mV)^2\}]$$

Here the adjustable parameters of fit were taken to be the intensity, I_{00}, and the position, $\tilde{\nu}_{00}$, of the (0,0) band, the Gaussian band width, b_g, and the ratio of (1,0) to (0,0) band intensities, X. The quantity V, representing the separation between bands, was assumed to be 1335 cm^{-1}, the value of the most intense band in the Raman spectrum of adenosine[29] which is expected to be the dominant totally symmetric vibrational mode in vibronic transitions. The summation was truncated after eight terms, and the curve fitting was restricted to wavenumbers less than about 40 000 cm^{-1}; quantitative analysis of the spectra at shorter wavelengths was deemed to introduce errors due to the proximity of the intense transitions making up the Y band of adenosine as revealed by the rapid change in the dichroic ratios in this region of the spectrum.

As the next approximation we allowed both progressions to be involved in both spectra with the restriction of using the same value of b_g for all bands in a given spectrum. The contribution of the minor progression to the absorption spectrum was found to be negligible (<0.1%); this result is fully consistent with the constancy of the measured dichroic ratios in this range of the spectrum. The contribution of the minor progression to the CD spectrum was found to be small but significant. The positions and relative

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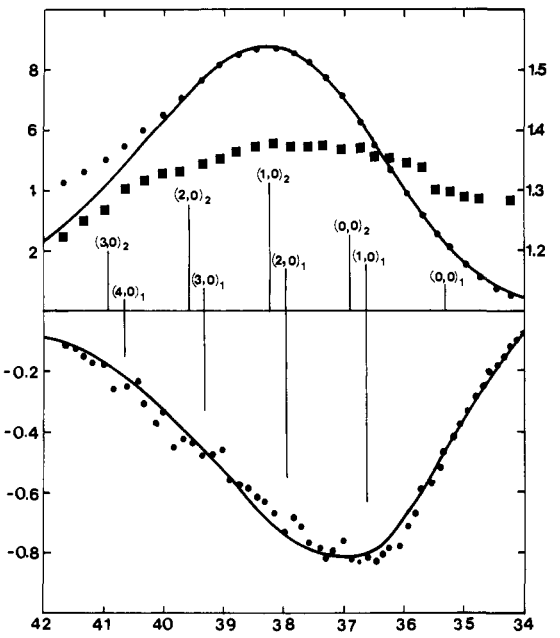

Figure 3. Spectra of a adenosine complexed with *cis*-diamminedichloroplatinum(II). Symbols, abscissa, and ordinate as in Figure 1.

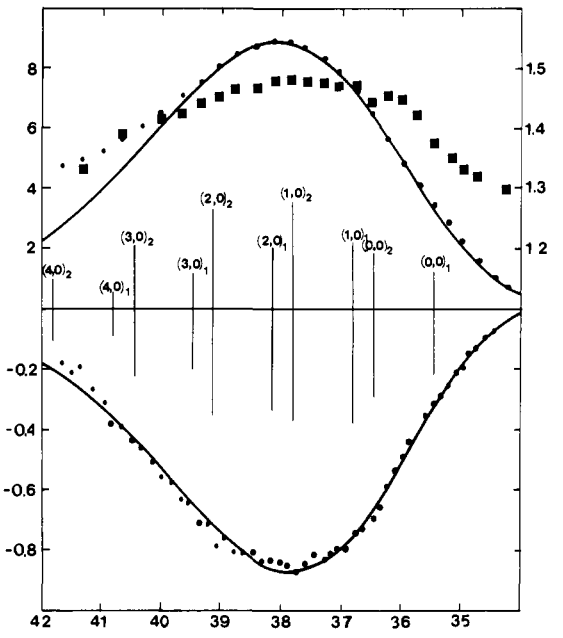

Figure 4. Spectra of adenosine complexed with *trans*-diamminedichloroplatinum(II). Symbols, abscissa, and ordinate as in Figure 1.

intensities of the individual bands corresponding to the best-fit parameters are shown by vertical lines in Figure 1. The relevant fitting parameters, the oscillator strengths, f, and rotatory strengths, R, are given in Table I. The latter two were calculated by using the following formulas:

$$f = 4.597 \times 10^{-9} b_g I_{00} \Sigma(x^m/m!)$$

$$R = 2.443 \times 10^{-39} b_g I_{00} \Sigma\{x^m/[m!(\bar{\nu}_{00} + mV)]\}$$

The first of these formulas has been derived;[27] the second follows from the definition of rotatory strength.[30]

The results of absorption and CD spectral measurements on AMP are shown in Figure 2 and summarized in Table I. The absorption spectrum is very similar to that of adenosine and seems to be due to the same vibronic transition which, in contrast to adenosine, dominates the CD spectrum of AMP as well.

As revealed by the behavior of the linear dichroism shown in Figures 3 and 4, the absorption spectra of the Pt complexes cannot be attributed to a single transition, even at wavenumbers below 40 000 cm^{-1}. The results of the curve fittings to two harmonic progressions are shown in the figures and Table I. In these calculations we retained the value V = 1335 cm^{-1}, since small changes in the vibrational energy on complexing to platinum (about 40 cm^{-1} for 9-methyladenine, for example[31]) would not significantly affect the fitting parameters.

Discussion

The method used to fit the spectral data at wavelengths longer than 250 nm to two vibronic progressions has ample precedence,[28,32,33] and it is theoretically superior compared with attempts to resolve spectra into, for example, pure electronic transitions of Gaussian shapes[14] on a wavelength scale. At wavelengths shorter than about 250 nm a third transition contributes both to the absorption and to the CD within the X band of adenosine as is apparent from a comparison of fitted and experimental results shown in Figures 1–4. Due to the low intensity of this transition relative to those both at lower and higher energies, a quantitative resolution into a unique progression was not attempted. However, it was estimated from a consideration of both the absorption and CD spectra of adenosine that the (0,0) band of this third transition is near 41 500 cm^{-1}; this figure fits previous experimental data[11,12,34] and theoretical calculations.[15] In the remainder of this discussion, attention will be directed at the region above 250 nm and, correspondingly, at the two lowest energy vibronic progressions within the X band.

Energies and Transition Moments. In adenosine and AMP the two vibronic transitions found above 250 nm are separated by about 700 cm^{-1} and the higher energy transition of the two carries the bulk of the absorption intensity. Both the positions and relative intensities are fully consistent with two (π^*,π) transitions predicted theoretically[4,5] and found experimentally in vapor phase[4,35] and single-crystal[34] studies. In addition, phosphorescence measurements on adenosine[9] and AMP[36] show the presence of a main progression with band separation of about 1300–1400 cm^{-1} and weak peaks appearing at multiples of 700 cm^{-1}, results which are in complete correspondence with our analysis. The suggestion that the lower energy transition may be (π^*,n) type[14] is not supported by experimental emission spectra,[9] linear dichroic spectra,[12] or a previous study of solvent effects on CD spectra.[13]

In the platinum complexes perturbation of the electronic structure of the adenine moiety produces shifts in the relative energies of the two progressions above 250 nm and, more significantly in this context, it increases substantially the absorptivity of the lower energy transition: consequently the linear dichroic spectra now demonstrate particularly well the presence of two transitions in this region of the spectrum. Compared with adenosine which has an essentially constant linear dichroism in the region of interest, the corresponding dichroic ratios of the platinum complexes show significant variations. Specifically, the transition moment of the higher energy progression is aligned toward the direction of stretch (dichroic ratio > 1) and that of the lower energy transition forms an angle toward the prependicular of the stretch direction as shown by the decrease of the dichroic ratios at the lower energy side of the spectra. Although an exact description of the orientation of small molecules embedded in stretched polymer films is complex,[37] they tend to orient with their long axes in the direction of stretch.[38] On this basis the observed linear dichroism across the spectra of adenosine and

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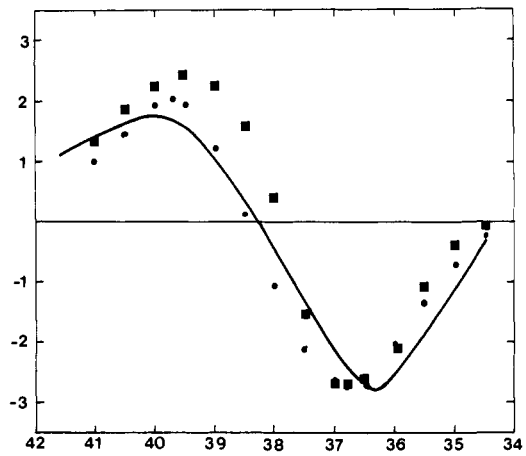

Figure 5. MCD spectrum of adenosine. Full line, calculated as explained in the text; circles, data extracted from Figure 4 of ref 10; squares, data extracted from Figure 2 of ref 13. Ordinate: $\Delta\epsilon$ (arbitrary units). Abscissa: $10^{-3}\tilde{\nu}$ (cm^{-1}).

its platinum complexes implies that the transition moment directions of the higher and lower energy progressions are oriented, more or less, along the molecular long and short axes, respectively; such an assignment fully conforms to the conclusions of single-crystal polarized spectral studies.[34] It also leads to some significant inferences.

First, it has been established that the complexing involves either the N_7 or the N_1 atom of adenosine.[39,41] We find (Table I) that the energy of the low-energy transition of adenosine is affected more by the binding of platinum ($\Delta\tilde{\nu} \sim 1000\ cm^{-1}$) than that of the high energy transition ($\Delta\tilde{\nu} \sim 200$–$600\ cm^{-1}$), and this implies that the favored binding position is at N_7, near the short axis rather than at N_1 situated along the long axis of the molecule.

Secondly, the Faraday effect on two near degenerate transitions with mutually perpendicular moments would result in large induced circular dichroism, or MCD, with equal magnitude but opposite sign contributions by the two transitions.[41] In Figure 5 we show by the continuous line the computed spectrum of adenosine taken to be the difference between the two fitted progressions normalized to equal intensities. In the same figure the points correspond to experimental data extracted from published MCD results on adenosine[10,13] and normalized to the magnitude of the calculated negative trough. The close agreement between experimental and calculated spectra seen in Figure 5 lends strong support to the proposed interpretation. We emphasize that according to this interpretation peaks and troughs observed in MCD spectra do not correspond to those of the individual transitions.

Thirdly, the resolution of the X band into transitions of known energies, dipole strengths, and directions constitutes a definitive test of the theories employed in calculating transitions monopoles and other not directly measurable quantities that play important roles in assessing both exciton and noncovalent interactions in nucleosides, polynucleotides, and nucleic acids.[17,43–46] Thus, for example, recent attempts to calculate CD spectra of adenine nucleosides by means of "regional" coupling schemes[45,47,48] may now be evaluated by considering how well the semiempirical wave functions, used for such calculations, are capable of reproducing the X-band spectrum.

Finally, as we shall now discuss, a simple rationalization of the observed circular dichroism of the X bands of adenine nucleosides emerges, providing a suitable framework for the interpretation of the CD of adenosine and related compounds.

Table II. CD Spectra of Anomeric Pairs of Adenine Nucleosides Fitted to Two Vibronic Progressions[14]

furanoside moiety	anomer	CD maximum, nm	$R^{(1)} \times 10^{40}$	$R^{(2)} \times 10^{40}$
lyxose	α	260	0.7	2.3
	β	257	0	−2.5
arabinose	α	258.5	0.2	2.5
	β	257.5	0	−4.2
xylose	α	258	0	5.3
	β	259.5	−0.5	−1.4
fibose	α	257	0	4.0
	β	264	−1.7	−0.6

Circular Dichroism. Comparison of Figures 1 and 2 shows that the absorption spectra of adenosine and AMP are essentially identical; however, the optical activities reside predominantly in the lower and higher energy transitions, respectively, in the two compounds. Both absorption and circular dichroism depend on the magnitude of the transition dipole but circular dichroism, in addition, is sensitive to conformation, that is, to the geometrical relation between the transitions in the base and the perturber sugar.[13,14,17,20] Because of this dependence on sugar-base geometry and in spite of the relatively large difference between their dipole strengths, either or both transitions may contribute significantly to the CD. Thus, changes in the positions of maxima and the overall shapes of the CD envelopes above 250 nm observed with adenosine nucleosides are to be attributed to changes in the relative contributions of the low- and high-energy transitions to the optical activity in this region. For example, we fitted the published CD spectra of anomeric pairs of D-pentofuranosides of adenine[14] to the two vibronic progressions; the results of this deconvolution, which we shall use subsequently, are given in Table II.

In considerations of nucleoside conformation an important role is played by the sugar–base torsion angle, ϕ_{CN}, defined as:[49] "the angle formed by the trace of the plane of the base with the projection of the C–O bond of the furanose ring when viewed along the C–N bond. This angle will be taken as zero when the furanose-ring oxygen atom is antiplanar to C_2 of the pyrimidine or purine ring, and positive angles will be taken as those measured in a clockwise direction when viewing from C to N". Previous empirical attempts to correlate the experimental CD of adenine nucleosides with ϕ_{CN}[50,51] are now to be amended by finding such correlations separately for the two transitions above 250 nm. The major problem with establishing such correlations is due to the existence of a range of conformers and corresponding ϕ_{CN} values in solution.[52,53] Thus, for example, adenosine itself may be present in both syn ($105° < \phi_{CN} < 195°$) and anti conformation ($-75° < \phi_{CN} < 15°$) in solution.[45] However, for some nucleosides steric hindrance due to substituents attached to C_2' and C_3' on the sugar moiety may severely restrict the range of possible torsion angles, and there is good agreement between theory[52] and experiment[54–57] concerning the possible extent of rotation about the glycosidic bond. Of the adenine nucleosides included in Table II, one may consider to be sterically restricted in the above sense all except

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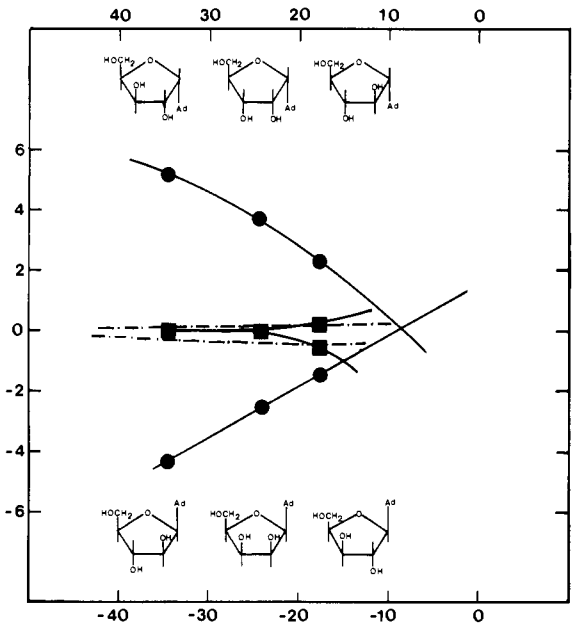

Figure 6. Correlation of rotatory strengths with glycosidic torsion angle. Circles, high energy, long-axis polarized transition; squares, low-energy, short-axis polarized transition. Full lines are the tentative correlations; broken lines are calculated correlations for the low energy transition. Ordinate: $R \times 10^{40}$ (cgs). Abscissa: top, ϕ_{CN} (α); bottom, ϕ_{CN} (β).

adenosine itself and the α-lyxose derivative. Following general conclusion of NMR and X-ray studies of adenine nucleosides,[58] we assigned an anti conformation to these compounds and determined[54] the sterically allowed torsion angles. We used the C_3' endo conformation for β anomers consistent with the majority of crystal structures of adenosine derivatives.[53] The range of ϕ_{CN} for the two sets of anomers were taken to be enantiomeric. We plotted in Figure 6 the rotatory strengths of the two transitions as a function of the midpoint of the estimated ϕ_{CN} range in the above nucleosides; the full lines correspond to the tentative correlations between these quantities. We note that a comparison of the CD spectra of β-arabinose and β-xylose nucleosides[14] with those of the corresponding 2'- and 3'-methyl-substituted derivatives[11] supports the contention that the restriction of ϕ_{CN} is essentially steric rather than being caused by specific interactions due to the hydroxyl groups.

The correlations shown in Figure 6 seem to be satisfactory when tested against other nucleosides. Thus, from the values of $R^{(1)}$ and $R^{(2)}$ of adenosine one finds a glycosidic torsion angle of near $-10°$ which may be considered to represent a reasonable weighted average of all conformers;[48] it is also close to ϕ_{CN} in the A-RNA conformation.[59] For AMP one estimates from Figure 6 a value of $\phi_{CN} \sim -22°$ which is near the expected, approximately fixed anti conformation due to interaction between the sugar phosphate and the adenine H_8 proton.[60,61] The correlations shown in Figure 6 also provide satisfactory interpretation of the observed CD spectra of the adenosine–platinum complexes. Accepting the reasonable suggestion that the bidentate cis platinum complex chelates the N_7 and 6-NH_2 positions of adenosine,[39] the positions of the amino groups of the complex may be considered fixed in the plane of the adenine moiety. Under such circumstances the binding of the cis platinum complex is expected to have little influence on the rotation about the glycosidic bond and the CD spectrum is correspondingly similar to that of uncomplexed adenosine. On the other hand, the monodentate binding of the trans platinum complex at the N_7 position brings into relatively close proximity the C_5' hydroxyl on the sugar and one of the amino groups of the complex. Thus interactions between these groups, in a way similar to AMP, reduces the average value of ϕ_{CN} and, as a result, both transitions contribute measurably to the observed Cotton effect.

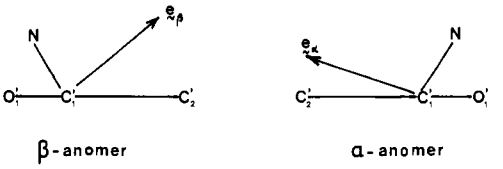

Figure 7. Effective moment directions in the furanose moiety. Both moments as well as the C_1'–C_2' bond are in the plane of the paper.

Finally we shall attempt to provide the theoretical basis of the correlations shown in Figure 6 in terms of the coupled oscillator theory[52] which has already been applied with success to conformational problems.[63,64] We shall use this theory in an elementary form: the CD is taken to be the result of the coupling between transition moments in the adenine moiety, the directions and magnitudes of which may be taken as known, and an effective moment induced by them in the sugar moiety. We shall not attempt to calculate the magnitude of CD, only the signs and trends, and accordingly the relevant formula is that for the "geometric factor" given by[47]

$$GF = \left[\mathbf{e}_1 \cdot \mathbf{e}_2 - \frac{3(\mathbf{e}_1 \cdot \mathbf{R})(\mathbf{e}_2 \cdot \mathbf{R})}{|\mathbf{R}|^2} \right] \cdot \frac{\mathbf{e}_1 \times \mathbf{e}_2 \cdot \mathbf{R}}{|\mathbf{R}|^3}$$

where $\mathbf{e}_1$ and $\mathbf{e}_2$ are unit vectors in the directions of the interacting transition moments and $\mathbf{R}$ is the vector connecting them. The adenine transition moments were treated as point dipoles and positioned at the center of the C_4–C_5 bond. The direction of the induced moment was assumed to be essentially independent of the type of pentose of the nucleosides considered here, at least for the same set of anomers. We then search for such an effective moment in the sugar moiety (positioned at C_1') whose interaction with the adenine transitions is able to reproduce the signs and trends in the CD shown in Figure 6.

It is well-known that the location of the transition moment vector influences the coupled oscillator calculations; indeed, transitions should not be localized at any particular point within the molecule. However, "regional" coupling schemes of bond–bond[47] or monopole–bond[45] types which are, in principle, better suited to evaluate interactions rely on the results of molecular orbital calculations to obtain the interacting molecular quantities. Unfortunately, depending on the particular form of the molecular orbital theory used and its parametrization, several sets of "monopoles" are available, for example, and in general they do not even add up to reproduce experimentally established transition moment directions. As a result and in spite of some ingenious attemps to adjust calculated quantities,[65] the choice between the various sets of quantities for the purposes of calculating CD spectra is neither obvious nor often justifiable. In view of the above and since we are concerned only with a justification of the trends observed in Figure 6, we consider the much less sophisticated procedure outlined above as adequate for our purpose. The additional assumption made that the effective moment induced in the sugar in approximately the same in each anomeric set finds support in theoretical calculations[17,44,48] and in considering experimental results on adenine nucleosides carring various substituents on the sugar;[11,13,66,67] provided the substituents are not

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likely to interfere with the range of sterically allowed ϕ_{CN}, the CD spectra of the corresponding nucleosides are very similar.

The calculations using the couple oscillators described above are straightforward; we found that only a very narrow range of effective moment direction is available that satisfies the requirement of giving the correct sign for the CD of the two transitions. The optimum results for the two transitions were normalized separately for comparison with the experimental rotatory strengths; these coincide with the correlation curves in Figure 6 for the long-axis transition but deviate somewhat from those for the short-axis transition as shown by the dashed lines in Figure 6. The induced moments used in these calculations for both sets of anomers point approximately from the C_1' to the C_2' atom forming an angle with the $O_1'C_1'C_2'$ plane as shown in Figure 7 where the C_1'–C_2' bond is drawn in the plane of the page. It is seen that the induced moments are at an approximately mirror-image relationship with respect to the base in the two sets of anomers; this would agree with the different sugar puckering known to be endo for the β anomers[53] and exo for the α anomers.[68] The additional difference in sugar backbone conformations due to the position of the C_5' atom may explain why the angles between the induced moment directions, $\mathbf{e}_\alpha$ and $\mathbf{e}_\beta$, and the C_1'-C_2' bond differ in the two sets of anomers.

The results demonstrate the usefulness of the simple coupled oscillator model: trends and signs of the CD of transitions in adenine as a function of ϕ_{CN} are reproduced at least as satisfactorily as a more sophisticated model used previously.[69] More important, these calculations demonstrate that CD spectra of the nucleosides studied in terms of two vibronic transitions above 250 nm is in total conformity with current theoretical concepts.

Conclusions

We resolved the X band of the adenosine into three vibronic transitions and were able to specify the positions, dipole strengths, and moments of the two lower energy transitions. We have shown that, in terms of these quantities, a wholly self-consistent interpretation may be given to both isotropic and anisotropic spectra of adenine nucleosides and platinum complexes of adenosine. The results described set a definitive experimental framework against which the results of theoretical calculations may be tested and quantitatively evaluated.

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The Oxygen Analogue of the Protonated Cyclopropane Problem. A Theoretical Study of the $C_2H_5O^+$ Potential Energy Surface[1]

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Abstract: Ab initio molecular orbital theory has been used to study the $C_2H_5O^+$ potential surface. Calculations have been carried out with basis sets up to the size of double-ζ plus polarization (6-31G^{++}) and with electron correlation incorporated at the levels of second (MP2) and third (MP3) order Møller–Plesset perturbation theory. Direct gradient techniques have been used to locate minima (corresponding to stable isomers) and saddle points (corresponding to transition structures) in the surface. Results at the various levels of theory are compared. The calculations predict that the most stable $C_2H_5O^+$ isomer is the 1-hydroxyethyl cation (**11**). Apart from the other experimentally observed isomers, viz., the methoxymethyl cation (**9**) and O-corner-protonated oxirane (**7**), the calculations predict that vinyloxonium ($CH_2CHOH_2^+$) (**12**) is also likely to be experimentally observable because of its low relative energy and high barrier to intramolecular rearrangement. O-Corner-protonated oxirane (**7**) is the only protonated oxirane structure which is found to be a minimum in the $C_2H_5O^+$ surface. Face-, edge-, and C-corner-protonated structures collapse without activation to other isomers. Likewise, the ethoxy cation ($CH_3CH_2O^+$) (**16**) and the 2-hydroxyethyl cation ($HOCH_2CH_2^+$) (**10**) are predicted not to be stable species.

Introduction

The structure of protonated cyclopropane is a subject which has aroused considerable experimental[2] and theoretical[3] interest. All calculations reported to date agree that the face-protonated form (**1**) lies considerably higher in energy than the edge (**2**)- and corner (**3**)-protonated structures. The most reliable calculations,[3f] carried out at the CEPA-PNO/DZP level on STO-3G optimized geometries, find the edge-protonated structure to lie lower in energy (by ~20 kJ mol^{-1}) than corner-protonated cyclopropane and to lie about 10 kJ mol^{-1} higher than the isopropyl cation, the lowest energy $C_3H_7^+$ isomer.

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