Hoffmann that predicts all of the results described above, even though their analysis was directed toward d^6 metallocycles and related systems. Two relevant conclusions from their theoretical calculations are (i) a trigonal-bipyramidal structure should be preferred if a single-faced π-donor (i.e. amide, NR_2^-) is present and (ii) strong σ-donors (i.e., alkyl ligands) will prefer the equatorial sites with a decrease in the angle between these donors (from 120° to 90°). This latter point is clearly apparent in the structure shown in Figure 3 wherein the C1–Ir–C2 angle is 76.0 (4)°. Thus, the replacement of a halide moiety, a good double-faced π-donor, with a strong σ-donor such as an alkyl ligand causes a sufficient perturbation to interchange the relative stabilities of the ground-state geometries for these five-coordinate d^6 complexes.

Equipped with the knowledge of the solution stereochemistry of these dialkyl derivatives, we are now in a position to address the mechanism of the photoinduced α-elimination process previously reported for these compounds.[13,18]

Acknowledgment. We thank NSERC and the Alfred P. Sloan Foundation for financial support. Johnson-Matthey is gratefully acknowledged for a generous loan of $IrCl_3$. We are also indebted to Dr. David L. Thorn for bringing ref 17 to our attention.

Supplementary Material Available: Experimental details, ^1H NMR data, and analytical data for all new compounds, tables of bond lengths, bond angles, and atomic positional and thermal parameters, ^1H NMR NOEDIFF experiment for 3, and a view of the structure of 3 down the P–Ir–P axis with the phenyl substituents removed for clarity (11 pages). Ordering information is given on any current masthead page.

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(18) In ref 13, the structures of the methyl alkyl complexes 3 and 4 are drawn as square pyramidal; this was our perception before we isolated the dimethyl derivative 2, with it's simple ^1H NMR spectrum, and before we had accumulated the NOE results.

Circular Dichroism of the Backbone and Side Chains Separated from Natural Circular Dichroism of Poly-L-tryptophan by the Fluorescence Detected Circular Dichroism Method

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Peggion and co-workers have concluded that poly-L-tryptophan (PLT) adopts a right-handed α-helical conformation in 2-methoxyethanol (2 ME).[1,2] The circular dichromism (CD) and optical rotatory dispersion (ORD) information presented by them indirectly suggests an α-helix of PLT in 2ME. However, it is difficult to assign directly a backbone conformation of PLT on the basis of the shape of the CD or ORD spectrum, as it contains side-chain contributions.

We succeeded in separating CD depending on the backbone contribution and on the side-chain contributions from natural CD of PLT (an average degree of polymerization of 30) in 2ME using the fluorescence detected circular dichroism (FDCD) technique, which was used to obtain the CD of a fluorescent chromophore.[3,4]

As a result, the shape of the separated backbone CD spectrum directly verified that PLT is α-helical in 2ME.

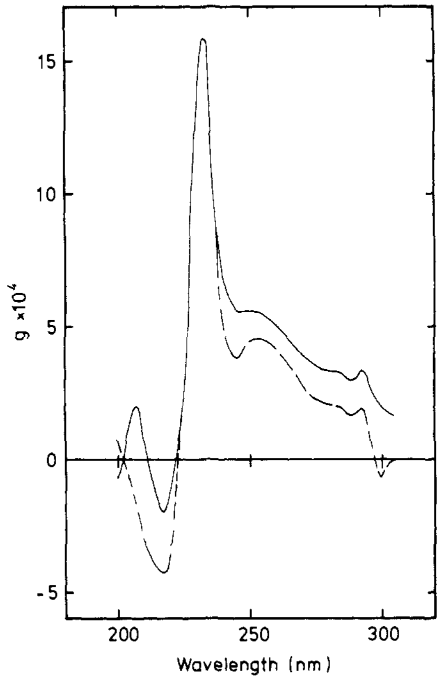

Figure 1. Spectra of fluorescence dissymmetry factor g_f (—) and absorpsion dissymmetry factor g_a (---) of PLT in 2ME. Error limits are roughly ±5 × 10^{-5}.

We report herein the conformational analysis of PLT using the FDCD method and significant information concerning the optical activity of PLT.

FDCD experiments were performed by using a JASCO J-500C spectropolarimeter, setting a solution filter (a 100-mm thickness of saturated aqueous solution of $NaNO_3$) between the sample cell and the photomultiplier for the elimination of the exciting circularly polarized light. The FDCD spectrum was obtained by scanning eight times with a 8-s time constant and averaging, using a JASCO DP-501 data processor. The spectra measurements were taken 3 times in a 0.5- or 1.0 mm-pathlength cuvette, and the obtained spectra were in good agreement with each other within the limit of experimental error. The FDCD base lines were measured with indole in 2-ME or DL-tryptophan in H_2O at pH 10. These base lines were coincident, and no base-line shifts were observed. PLT fluorescence was essentially depolarized ($P < 0.06$) below 295 nm.

Figure 1 compares the fluorescence dissymmetry factor g_f obtained from the FDCD experiments with the absorption dissymmetry factor g_a obtained from the ultraviolet absorption and CD spectra. The distinction between the shapes of these two dissymmetry factor spectra indicates that the separation of CD of its fluorophores from natural PLT CD have been accomplished by the FDCD technique.

It is reasonable to consider that PLT optical activity may originate from a one-electron mechanism μ1–m1; the electric and magnetic-dipole transitions of the chromophore, such as indole chromophores ^1B_a, ^1B_b, ^1L_a, ^1L_b and amide chromophores n–π^*, π–π^*, are mixed by the static Coulombic field of the other groups, and from a dynamic coupling mechanism μ1–μ2; electric dipole interactions of amide–amide, amide–indole, and indole–indole chromophores.[5,6]

However, on the following assumptions we tried to separate the backbone CD, coming from amide chromophore contributions, and the side-chain CD, coming from indole chromophore contributions, from natural CD of PLT using the eq 1 and 2.

$$\Delta\epsilon_{side} = g_f\epsilon_{PLT} \qquad (1)$$

$$\Delta\epsilon_{back} = \Delta\epsilon_{PLT} - \Delta\epsilon_{side} \qquad (2)$$

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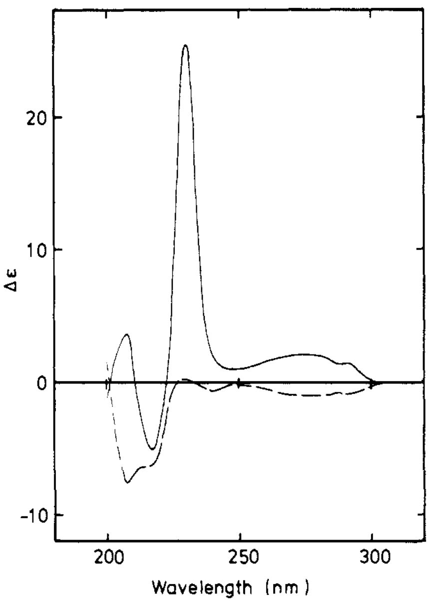

Figure 2. CD spectra of side chains (—) and backbone (---) separated from natural CD of PLT in 2ME by the FDCD technique. The $\Delta\epsilon$ values are expressed in term of the concentration of residues in cm^{-1} M^{-1}.

where $\Delta\epsilon_{\mathrm{PLT}}$, $\Delta\epsilon_{\mathrm{side}}$, and $\Delta\epsilon_{\mathrm{back}}$ are the molar CD of PLT, side chain, and backbone, respectively. ϵ_{PLT} is the molar extinction coefficient of PLT. It was assumed that little interactions of $\mu1$–$\mu2$ between amide and indole chromophores exist and that amide chromophores are not fluorophores and energy transfers between amide and indole chromophores are negligible. Furthermore, the assumption was made that the absorpsion of PLT above 200 nm is almost solely due to the indole chromophores.[7]

Figure 2 shows the resultant spectra of $\Delta\epsilon_{\mathrm{side}}$ and $\Delta\epsilon_{\mathrm{back}}$. The shape of the backbone CD spectrum closely resembles that of a typical α-helical CD spectrum.[8] This verifies that PLT adopts a right-handed α-helical conformation in 2ME and shows that the above assumptions are reasonable.

The formation of the negative dichroic band for the backbone in the ^{1}L region is of interest. In the ^{1}L region, no CD bands exist for the separated backbone CD spectrum (if the optical activity in this region originates from only one fluorescent species) because of no contribution of the amide chromophores here. However, if more than one optically active fluorescent species i, such as ^1L_a and ^1L_b transitions, is present, and the quantum yields Φ_i of these species are different from each other, then the g_f value obtained from FDCD experiment is expected to behave according to eq 3.[3] The g_f is not in agreement with $\Delta\epsilon_{\mathrm{PLT}}/\epsilon_{\mathrm{PLT}}$.

$$g_f = \frac{\sum_i \Phi_i \Delta\epsilon_i}{\sum_i \Phi_i \epsilon_i} \tag{3}$$

When taking into account the possibility of energy transfer between these species, the g_f value is expressed more complicatedly.[3] Therefore, the origin of the negative CD band for the backbone in the ^{1}L region is due to the difference between $\Delta\epsilon_{\mathrm{PLT}}/\epsilon_{\mathrm{PLT}}$ and the g_f value.

A negative CD band at around 240 nm for the backbone may be produced for the same reason as mentioned above.[9,10] In this region, the overlapping of the ends of ^1L_a and ^1B_b absorption bands is expected. Of course we cannot deny the possibility of the contribution of amide chromophores in this band. Our FDCD experiments did not indicate the existence of a ^{1}C symmetry-forbidden transition of indole chromophore.[11]

The side-chain CD obtained indicates that a positive intense CD band at 230 nm, whose pair is an ~217-nm negative band, originates from the formation of exciton coupling between indole chromophores. Moreover, the greatly different intensities of these two exciton bands and the existence of an ~207-nm positive band show that the $\mu1$–$\mu2$ mechanism may not only occur between ^1B_b transitions but between ^1B_a and ^1B_b transitions.

A more detailed investigation for optical activity of PLT is now in progress by our group.

Our FDCD technique for PLT can be applied to the conformational analysis of similar peptides such as poly-L-tyrosine.

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Thioxanthones as High Turnover Catalytic Templates in Directed Chlorination Reactions

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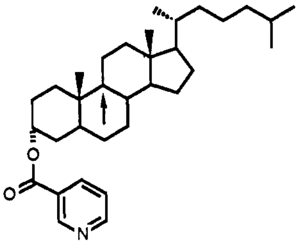
We have recently reported[1] that the steroid nicotinate ester **1** is catalytically chlorinated at C-9 by forming a mixed complex with Ni^{2+} or Cu^{2+} and template **2**. Then PhICl$_2$, with irradiation, starts a chain process in which a chlorine atom is first transferred to the template and then attacks the steroid hydrogen, in a radical relay[2] mechanism. Remarkably, under appropriate conditions the catalyst **2** undergoes 10^9 turnovers.



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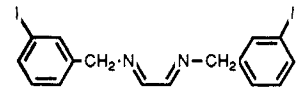

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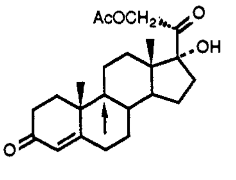

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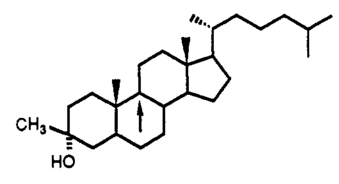

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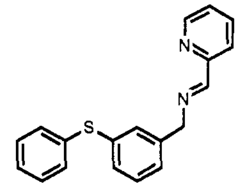

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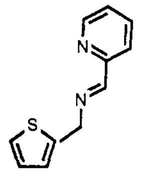

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