zation in so far as that effect is measured by magnetic properties. Although such an insensitivity to atomic position would be expected for nonaromatic molecules, and has been demonstrated for cyclopent-2-en-1-one and cyclopent-3-en-1-one,[21] this appears to be the first demonstration in aromatic systems. Comparison of the oxazole and isoxazole results is noted to depend on the assumption that the local atom values are independent of the neighboring atoms more than for the cyclopentenone case. While this appears to be a valid assumption,[20] it is still open to question.

The relationship between magnetic and other criteria of aromaticity is of current interest.[22] A thermodynamic comparison of imidizole and pyrazole, molecules related to 1 and 2 by the replacement of oxygen by nitrogen, has been reported in which imidizole is assigned approximately one-half the resonance energy of pyrazole.[23] By the magnetic criterion no large difference exists in the electron delocalizations in oxazole and isoxazole.

An examination of the nonlocal values of the magnetic susceptibilities indicates that oxygen has a more significant effect than double-bonded nitrogen on suppressing the magnetic effects of delocalization. Comparison of benzene to pyridine and of furan to oxazole and isoxazole reveals a decrease in the nonlocal contribution of about 20% for the nitrogen-containing molecules, but this decrease is less than the experimental uncertainty. However, furan, oxazole, and isoxazole all seem to have significantly smaller contributions than the other six π-electron systems although substantial delocalization is still indicated.

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Optical Rotatory Power in the Ground State and Electronically Excited State of Diketopiperazines Containing Aromatic Side Chains

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Contribution from the Department of Chemical Physics, The Weizmann Institute of Science, Rehovot, Israel. Received May 15, 1974

Abstract: The circular dichroism and the circular polarization of the fluorescence of various cyclic dipeptides containing aromatic side chains has been studied. The optical rotatory power deduced from these measurements vanished upon electronic excitation in fluid media but is essentially the same in the ground and electronically excited states in highly viscous media. A change in conformation thus occurs upon excitation in fluid solution essentially before light emission takes place. The change responsible for the disappearance of the optical activity is faster than the rate of rotational relaxation as monitored by the linear polarization of the fluorescence.

The conformation of diketopiperazines has been the subject of a variety of studies. On the theoretical side, molecular orbital calculations performed for *cyclo*(Gly-Phe) predict a folded conformation for this compound.[1] Empirical energy calculations on *cyclo*(Gly-Phe), *cyclo*(Gly-Tyr), and *cyclo*(Gly-Val) also indicate that the minimum energy conformations have the side chains stacked over the piperazine ring.[2] Such conformations for cyclic dipeptides were deduced experimentally from X-ray structure analysis[3] and nmr[4,5] studies and gained support from CD measurements.[6,7]

The above studies are concerned with the molecular conformation of the cyclic dipeptides in the electronic ground state. Since the electronic charge distribution in an excited chromophore is different from that in the chromophore in the ground state, the interaction of the chromophore with its environment in the two states may be very different. The equilibrium conformation of the cyclic dipeptides with aromatic side chains may thus change upon electronic excitation of the aromatic chromophores. The lifetime of the excited chromophores (which falls in the nanosecond time range) is long enough to permit partial or complete relaxa-

tion of the molecular geometry to the new equilibrium conformation in fluid media at room temperature before light emission occurs from the excited molecule. The properties of the fluorescence are thus related to the conformation of the emitting molecule in the excited state in the same way that the absorption properties are related to the molecular conformation in the ground state. If the excited molecule relaxes to its excited equilibrium conformation with a relaxation time that is comparable in magnitude to the lifetime in the excited state, the fluorescence properties will be different when measured at different times following excitation. Such changes in the fluorescence spectrum with time were indeed reported recently for *cyclo*(Gly-Trp) and *cyclo*(Ala-Trp).[8] These results were interpreted in terms of a model which assumed two conformations for the cyclic peptides: the folded form and the extended form, the former relaxing to the latter upon electronic excitation with a lifetime of the order of 10^{-8} sec.

In the study to be reported below we have probed the change in molecular conformation which occurs upon electronic excitation of cyclodipeptides containing benzene, phenol, and indole side chains by the optical rotatory power of these substances in the ground and excited states. It has been recently shown that the circular polarization of luminescence, CPL, is a measure of the optical activity of the emitting molecule in the excited state in much the same way that circular dichroism, CD, is a measure of the optical activity in the ground state.[9-16] A comparison of the CD and CPL spectra of the cyclic dipeptides studied shows that in fluid media a very fast change in conformation occurs essentially before any light emission takes place. This change in conformation is arrested in highly viscous media.

Experimental Section

Materials. The cyclic dipeptides (*cyclo*(Gly-L-Tyr); *cyclo*(L-Tyr-L-Tyr); *cyclo*(L-Trp-L-Phe); *cyclo*(L-Trp-L-Tyr); *cyclo*(L-Trp-L-Trp); *cyclo*(L-Trp-L-Val); and *cyclo*(L-Trp-D-Val)) were a gift of Professor M. Wilchek, the Weizmann Institute of Science. The method of preparation of the cyclic peptides has been described before.[6] The method of preparation and of optical resolution of 1,1'-bianthracene-2,2'-dicarboxylic acid has been presented elsewhere.[9] Dioxane, chloroform, glycerol, and DMSO were of spectro grade. Cellulose acetate, polyoxypropylene, and poly(methyl methacrylate) were a gift of Mr. S. Gassner of the Weizmann Institute of Science.

Methods. Absorption spectra were obtained with a Zeiss Model PMQ II spectrophotometer. Corrected fluorescence spectra were measured with a Turner Model 210 spectrofluorimeter. Circular dichroism was measured with a Cary Model 60 spectropolarimeter, with a 6002 CD attachment. The linear polarization of the fluorescence was measured with an instrument of the type described by Weber,[17] built by Dr. M. Shinitzky, the Weizmann Institute of Science. The circular polarization of the fluorescence was studied with an instrument designed and built in our laboratory.[18] A high pressure mercury lamp (HBO 100W/2, Osram) was used for the excitation of the fluorescence. The excitation light was monochromated with a Bausch and Lomb high intensity monochromator, set to 254 or 275 nm, and filtered with an interference filter (Pomfret, special order, band pass 250-290 nm) to remove stray light. The fluorescence light was monochromated with a Jarrell-Ash double monochromator (Model 82-410), with spectral resolution of 15 nm. A cut-off filter (1 cm optical length, sodium biphthalate 0.1 M solution) was used in conjunction with the monochromator to remove stray light due to the excitation beam. An elasto-optic light modulator (Morvue, Model PEM-3) was used to modulate the circularly polarized component in the fluorescence light. The instrument was calibrated as described.[18]

Highly viscous solutions of the fluorescent materials studied were prepared in concentrated solutions of high molecular weight polymers: poly(methyl methacrylate) in chloroform, cellulose acetate in dioxane, or polyoxypropylene in dioxane. The procedure was as follows: the fluorescent material was dissolved in the chloro-
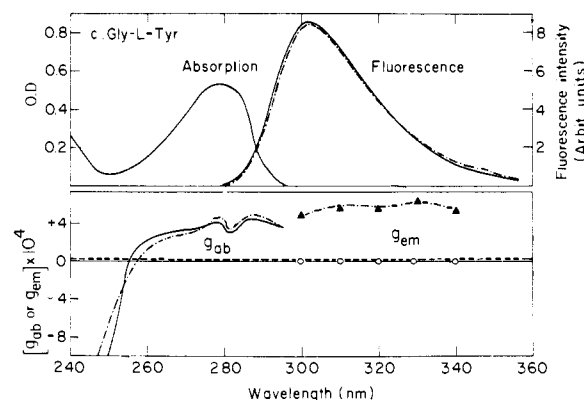

Figure 1. Spectroscopic data for *cyclo*(Gly-L-Tyr). Absorption: in dioxane solution (3.8×10^{-4} M) (—); a very similar spectrum was obtained in a highly viscous solvent composed of polyoxypropylene and dioxane (POP-D). Fluorescence: in dioxane (3×10^{-5} M) (—); in POP-D ($\cdot$ - $\cdot$). Absorption anisotropy factor, g_{ab}: in dioxane (3.8×10^{-4} M) (—); in POP-D ($\cdot$ - $\cdot$). Emission anisotropy factor, g_{em}: in dioxane (3.8×10^{-4} M) (O); in POP-D (▲). For comparison, g_{ab} and g_{em} of L-Tyr in dioxane or POP-D (- - -). Room temperature (~22°).

form or dioxane; the polymer was then added in small portions while the solution was stirred on a hot water bath. The solvent was then partially evaporated in a water bath, and the hot viscous solution was subsequently transferred to the fluorescence cell. The cell was kept in a hot water bath till all air bubbles were removed and was then allowed to cool to room temperature for a few hours. The viscosity of the solution was so high that it could hardly flow at room temperature. The cell and its contents were checked between crossed polarizers to ascertain that they exhibited no perceptible birefringence.

The data on the circular dichroism and the circular polarization of the luminescence are expressed by the absorption and emission anisotropy factors, g_{ab} and g_{em}, respectively. These factors are defined as $g_{ab} = (\epsilon_l - \epsilon_r)/[(\epsilon_l + \epsilon_r)/2]$ and $g_{em} = \Delta f/(f/2)$, where ϵ_l and ϵ_r are the absorption coefficients for left-handed and right-handed circularly polarized light, respectively, and $\Delta f/f$ is the fraction of circularly polarized light in the fluorescence (Δf being defined as positive for left-handed circular polarization). If the molecular conformations in the ground state and in the first singlet excited state (from which the fluorescence occurs) are identical, g_{ab} for the long wavelength absorption band and g_{em} should assume the same sign and numerical value.[16]

Results and Discussion

The fluorescence and absorption spectra, as well as the spectral variation of the absorption and emission anisotropy factors, g_{ab} and g_{em}, respectively, are presented in Figures 1-7 for a variety of cyclic dipeptides. The following substances were studied: *cyclo*(Gly-L-Tyr), *cyclo*(L-Tyr-L-Tyr), *cyclo*(L-Trp-L-Phe), *cyclo*(L-Trp-L-Tyr), *cyclo*(L-Trp-L-Trp), *cyclo*(L-Trp-L-Val), and *cyclo*(L-Trp-D-Val). The absorption and CD spectra are in good agreement with those that were published before[6] for a few of the above substances. It may be noted that L-tyrosine (see Figure 1) and *N*-acetyl-L-tryptophanamide (see Figure 6) as well as the short peptides L-Trp-(Gly)₃-COOH, carbobenzoxy-(Gly)₃-L-Trp(Gly)₃-O-benzyl ester and carbobenzoxy-(Gly)₄-L-Trp-(Gly)₃-O-benzyl ester show negligible CD or CPL. Some linear dipeptides (L-Tyr-L-Tyr, L-Trp-L-Tyr, L-Trp-L-Trp, and L-Tyr-L-Trp) were shown to possess a CD spectrum which is much smaller than that of the corresponding cyclic dipeptides.[6] Interaction of the aromatic side chains with the piperazine ring is thus indicated. If two side chains are present, some mutual interaction is also indicated. Thus, the CD of *cyclo*(Gly-L-Tyr) and *cyclo*(L-Tyr-L-Tyr) are not identical (Figures 1 and 2; see also ref 6), and the CD of *cyclo*(L-Trp-L-Val) and *cyclo*(L-Trp-D-Val) are quite different (Figures 6 and 7).
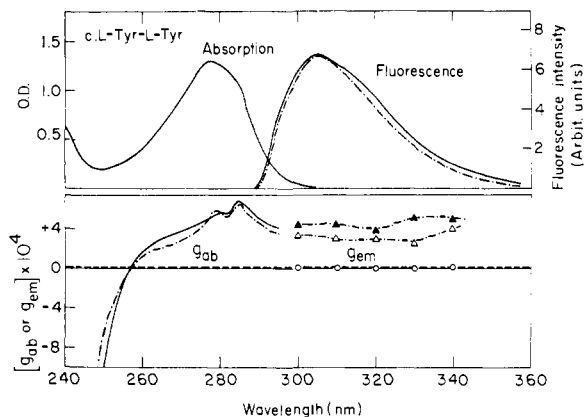
Figure 2. Spectroscopic data for *cyclo*(L-Tyr-L-Tyr). Absorption: in dioxane solution (6×10^{-4} M) (—); a very similar spectrum was obtained in POP-D. Fluorescence: in dioxane (4×10^{-5} M) (—); in POP-D (- · -). Absorption anisotropy factor, g_{ab}: in dioxane (6×10^{-4} M) (—); in POP-D (- · -). Emission anisotropy factor, g_{em}: in dioxane (6×10^{-4} M) (O); in POP-D (▲); in a highly viscous solvent composed of cellulose acetate and dioxane (△). For comparison, g_{ab} and g_{em} of L-Tyr in dioxane or POP-D (- - -). Room temperature ($\sim 22°$).
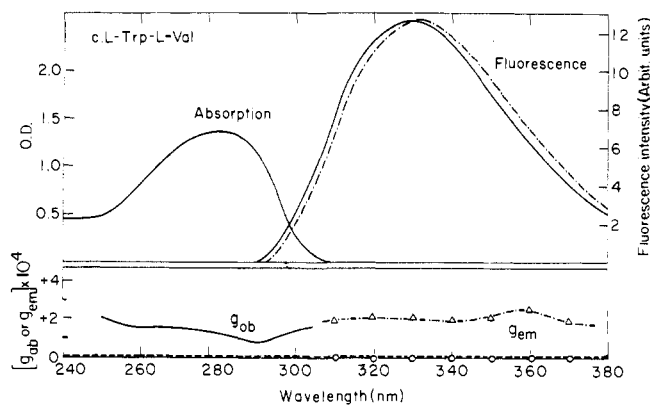

Figure 3. Spectroscopic data for *cyclo*(L-Trp-L-Val). Absorption: in dioxane solution (2.5×10^{-4} M); a very similar spectrum was obtained in a highly viscous solvent composed of POP-D. Fluorescence: in dioxane (1.5×10^{-5} M) (—); in POP-D (· - ·). Absorption anisotropy factor g_{ab}: in dioxane (2.1×10^{-4} M) (—). Emission anisotropy factor, g_{em}: in dioxane (5×10^{-4} M) (O); in POP-D (△). For comparison, g_{ab} and g_{em} of N-acetyl-L-tryptophanamide in dioxane and in POP-D (- - -). Room temperature ($\sim 22°$).

The most striking finding described in Figures 1-7 is the fact that whereas all the cyclic dipeptides studied show a finite value for the absorption anisotropy factor in dioxane solution at room temperature, their emission anisotropy factor is zero within experimental error (estimated to be $\pm 3 \times 10^{-5}$) under the same condition. The same results were obtained for diketopiperazines dissolved in DMSO. Since g_{ab} at the long wavelength band of the absorption spectrum is expected to have the same value as g_{em} if the molecular conformation is the same in the ground state and the electronically excited state,[15] it is obvious that a change has occurred in the conformation of the molecules of all the substances studied. This change has taken place following electronic excitation but before any appreciable amount of light has had a chance to be emitted. These results cannot be reconciled with the model proposed by Donzel, et al.,[8] according to which the diketopiperazines exist in either of two conformations: the folded form and the extended form. According to this model the two forms are at equilibrium in the ground state but a change in the equilibrium constant occurs upon electronic excitation, resulting in a shift in the
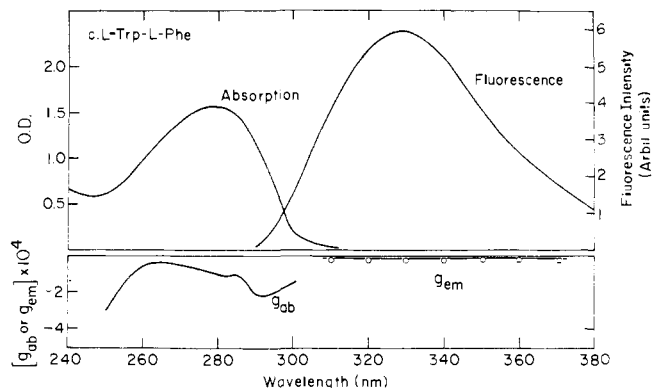

Figure 4. Spectroscopic data for *cyclo*(L-Trp-L-Phe). Absorption: 2.7 $\times 10^{-4}$ M in dioxane. Emission: 3×10^{-5} M in dioxane. Absorption anisotropy factor, g_{ab}, and emission anisotropy factor, g_{em}: 2.7×10^{-4} M in dioxane ($\sim 22°$).
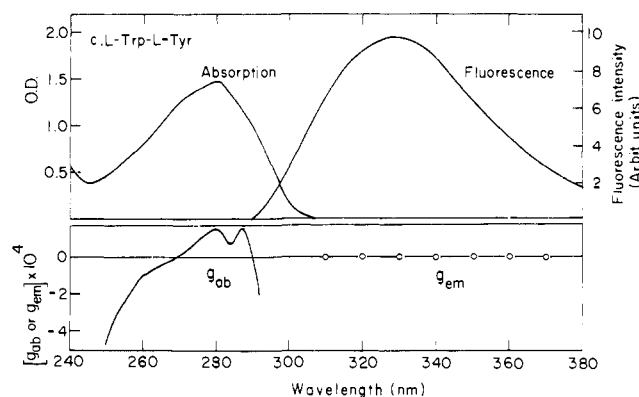

Figure 5. Spectroscopic data for *cyclo*(L-Trp-L-Tyr). Absorption: 2.2 $\times 10^{-4}$ M in dioxane. Emission: 2×10^{-5} M in dioxane. Absorption anisotropy factor, g_{ab}, and emission anisotropy factor, g_{em}: 2.2×10^{-4} M in dioxane ($\sim 22°$).

relative concentrations of the two forms during the lifetime of the excited state. The spectrum of the fluorescence emitted a short time after excitation has thus been assumed by the above authors to be due to the equilibrium mixture characteristic of the ground state. The present study shows, however, that the fluorescence light does not reflect any rotatory power of the emitting molecules which resembles that of the ground state molecules. Moreover, g_{em} does not show any variation across the spectrum, which one would expect to happen if the fluorescence is made up of two different spectra of emitting molecules with different conformations.[16]

The above conclusion that the difference between g_{ab} at the red edge of the absorption spectrum and g_{em} is due to a change in molecular conformation which takes place subsequent to electronic excitation was further verified by repeating some of the above experiments in solutions of extremely high viscosity. In viscous media relaxation of molecular conformation is expected to be impeded and possibly arrested within the period between excitation and light emission. The results are included in Figures 1, 2, and 6. When *cyclo*(Gly-L-Tyr), *cyclo*(L-Tyr-L-Tyr), and *cyclo*(L-Trp-L-Val) were studied in highly viscous solutions of polyoxypropylene in dioxane, POP-D, g_{em} was found to assume a finite value of very similar magnitude as g_{ab} at the long wavelength edge of the absorption spectrum. The value of g_{ab} was very similar in dioxane and in POP-D. *cyclo*(L-Tyr-L-Tyr) was also studied in a highly viscous solution of cellulose acetate in dioxane with similar results; study in this solvent system would not, however, by itself contribute
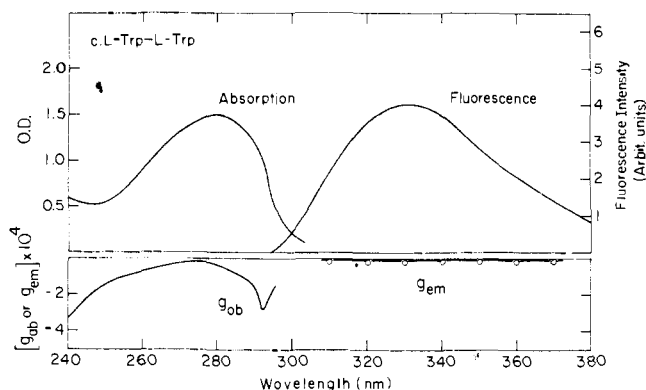
Figure 6. Spectroscopic data for *cyclo*(L-Trp-L-Trp). Absorption: 1.4 × 10⁻⁴ M in dioxane. Emission: 2 × 10⁻⁵ M in dioxane. Absorption anisotropy factor, g_{ab}, and emission anisotropy factor, g_{em}, in dioxane; 1.4 × 10⁻⁴ M (~22°).
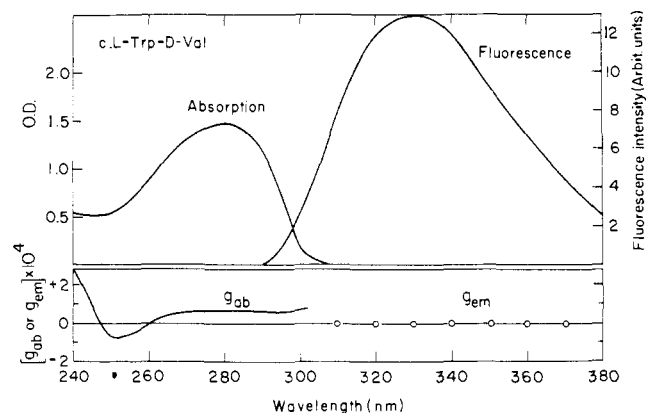

Figure 7. Spectroscopic data for *cyclo*(L-Trp-D-Val). Absorption: 2.65 × 10⁻⁴ M in dioxane. Emission: 4 × 10⁻⁵ M in dioxane. Absorption anisotropy factor, g_{ab}, and emission anisotropy factor, g_{em}, in dioxane; 2.65 × 10⁻⁴ M (~22°).

definite proof to the point under discussion since the polymer is asymmetric and could conceivably induce asymmetry in the dissolved cyclic dipeptide. It may be noted that L-Tyr and *N*-acetyl-L-Trp-amide did not show any measurable CPL in the highly viscous solvent.

It is of interest to point out that while g_{ab} varies markedly with wavelength, g_{em} exhibits only slight variation across the emission spectrum. This difference may be rationalized in terms of the theorem pointed out by Moscowitz[16,19] which states that the anisotropy factor across a single electronic transition should to a first approximation assume a constant value for allowed transitions. While the absorption spectrum involves various electronic transitions, the fluorescence in condensed media usually involves a single electronic transition and is thus expected to be associated with a constant anisotropy factor for allowed transitions of pure substances.[16]

The linear polarization of *cyclo*(L-Trp-L-Val) was measured in dioxane and in glycerol. The results are shown in Figure 8. As seen in this figure, the fluorescence is completely depolarized in dioxane; *i.e.*, the rotational relaxation of the excited chromophore is practically complete in this solvent during its lifetime. On the other hand, the fluorescence emitted in glycerol solution exhibits an appreciable amount of linear polarization at room temperature (22°) indicating that the rotational relaxation of the excited chromophore in this solvent is only partial in the interval of time between light absorption and emission. For comparison, the linear polarization in glycerol at −25° is also included in
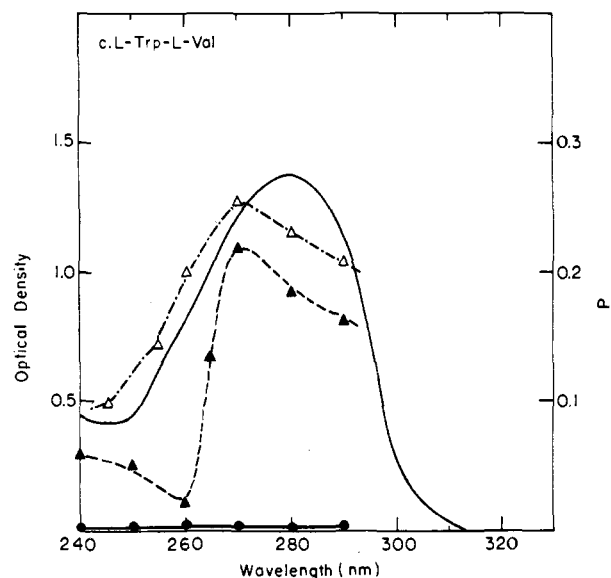

Figure 8. Spectrum of *linear* polarization of *cyclo*(L-Trp-L-Val) in glycerol. $p = (I_{\parallel} - I_{\perp})/(I_{\parallel} + I_{\perp})$, where $I_{\parallel}$ and $I_{\perp}$ are the fluorescence intensities observed through a polarizer oriented parallel and perpendicular, respectively, to the direction of the polarization of the excitation beam. Concentration: 5 × 10⁻⁵ M; (●) In dioxane at room temperature (~22°); (▲) in glycerol at room temperature (~22°); (△) in glycerol at −25°. Included is the absorption spectrum in dioxane (—), 2.5 × 10⁻⁴ M.
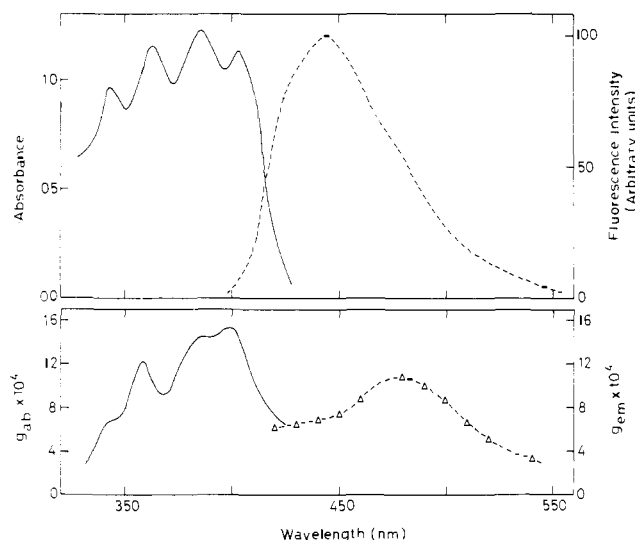

Figure 9. Spectroscopic data for L-1,1′-bianthracene-2,2′-dicarboxylic acid in a highly viscous solvent composed of poly(methyl methacrylate) in chloroform. Upper: absorption (—) and emission (- - - -) spectra. Lower: absorption anisotropy factor, g_{ab} (—), and emission anisotropy factor, g_{em} (- - - -). Room temperature ~22°.

Figure 8. However, g_{em} in glycerol is zero within experimental error. It is thus obvious that complete rotational relaxation is not necessary in order to abolish the optical activity of the electronically excited molecule. These results further show that the conformational changes which cause g_{em} to be different from g_{ab} occur much faster than the rotational relaxation time of the molecules.

The above results regarding the magnitude of the optical activity of the cyclic dipeptides studied may be of value in the theoretical calculation of their conformation in the excited state. Such use of the circular polarization of fluorescence has already been made in the evaluation of the conformation of 1,1′-bianthracene-2,2′-dicarboxylic acid in the excited state. The CD and CPL of this compound was stud-

ied previously[9] and the results have been applied to the evaluation of the dihedral angle between the two anthracene rings in the ground and electronically excited states.[20] The values obtained are 85-100° at the ground state and 75 ± 5° or 113 ± 5° at the excited state (two different values can be assigned to the dihedral angle in the excited state to fit the experimental data). Also in this case the anisotropy factors of absorption and emission assume equal magnitude at the overlap region of absorption and emission when studied in a very highly viscous mixture of poly(methyl methacrylate) in chloroform (see Figure 9), which indicates a freezing of the ground state conformation by the viscous solvent.

Conclusion

The optical rotatory power of all the seven cyclic dipeptides studied is different when in the ground state and in the electronically excited state, indicating a difference in molecular conformation in the two states. The change in conformation reflected by the optical activity is very fast compared to the fluorescence decay rate even in glycerol but is arrested in extremely highly viscous solvents. Overall rotational Brownian motion of the excited chromophores, as reflected by the linear polarization of the fluorescence, is shown to be a different and slower process, since it is appreciably hindered in glycerol. The relaxation processes observed by Donzel, et al.,[8] in the nanosecond time range in fluid media seem to be still slower processes of a still different nature, since they were observed under conditions where rotational relaxation is complete within the fluorescence

lifetime. We could not detect any linear polarization in dioxane solution.

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Spectra and Structure of Organogermanes. XVII.[1] Microwave Spectrum, Structure, Dipole Moment, and Internal Rotational Barrier of Vinylgermane

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Abstract: The microwave spectra of ten isotopic species of vinylgermane have been recorded in the region between 12.4 and 40.0 GHz. From a least-squares fit of the 25 rotational constants and an assumed structure for the vinyl group, except for the C=C bond distance, the following structural parameters were calculated: $r(C=C) = 1.347Å, r(Ge—H) = 1.521Å, r(Ge—C) = 1.926Å, \angle(CCGe) = 122°54', \angle(CGeH) = 110°42'$. The barrier to internal rotation of the germyl group has been determined to be 1238 ± 57 cal/mol from the ground and excited state splittings of the rotational transitions. Quadratic Stark effect measurements on the $J = 3 \leftarrow 2$ transitions gave $|\mu_a| = 0.49 ± 0.02, |\mu_b| = 0.12 ± 0.02$, and $|\mu_{total}| = 0.50 ± 0.03$ D. An upper limit of 2.8 MHz has been set on the quadrupole coupling constant, $|\chi_{aa}|$, for ^{73}Ge isotope from a measurement of the line width of the transitions due to this isotopic species.

There have been few structural studies of organogermanium compounds in the gaseous state[4-12] although there have been some rather large variations reported[13] for the Ge–C distances for some of these compounds. As a continuation of our earlier studies of a series of organogermanes, we have investigated the microwave spectrum of vinylgermane. From vibrational studies[14] on CH_2CHGeH_3 and CH_2CHGeD_3, it was concluded that the molecule has C_s symmetry. However, no torsional frequency for the germyl group was observed for either molecule.

The microwave spectra of propylene[15-17] and vinylsilane[18] have been investigated and their structures and bar-

riers to internal rotation were determined. The relatively large difference in barriers between ethane[19] (2.93 kcal/mol) and propylene[17] (1.98 kcal/mol) vs. the small difference in barriers between methylsilane[20] (1.67 kcal/mol) and vinylsilane[18] (1.50 kcal/mol) has been attributed to hyperconjugation. A comparison of the dipole moment and the corresponding C–C single bond distances in ethane and propylene also tends to favor hyperconjugation in propylene. Since the microwave spectrum of methylgermane[4-6] was investigated and its structure, barriers to internal rotation, and electric dipole moment were determined, it was felt that the study of the microwave spectrum of vinylgermane might