Photoresponsive Peptide and Polypeptide Systems. Part 7.[1] Reversible Chiral Photochromism and Solubility Change of Azo Aromatic L-Lysine Related Compounds

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Disubstituted azo aromatic L- and D-lysine homologues with one to four methylene groups in the side chain, and related compounds, have been synthesized. The photochemical properties of the azo aromatic lysine series have been studied from both achiral and chiral standpoints. On irradiation at different wavelengths, the azo aromatic lysine series change their solubilities achirally in certain solvents, being soluble under u.v. light (*cis*) and precipitating out under visible light (*trans*). The dipole moments of the solvents used are considered to be important in this solubility change. The chiral photochemical properties of the above lysine related compounds have been examined by absorption and circular dichroism (c.d.) spectroscopy. The whole c.d. spectrum exhibits reversible photochromism on irradiation with light, owing to the *trans-cis* photoisomerization of the azo aromatic moieties. The exciton chirality method has been successfully applied in order to demonstrate the origin of the dichroic bands in the 260–390 nm wavelength region which exhibit coupling of the transition dipole moment due to the *trans* π–π^* transition of the azo aromatic chromophore under an asymmetric C_α carbon environment.

Photochromic peptides and polypeptides are interesting systems because of their relevance to the molecular mechanism of photoreguration in biological materials and processes.[2–4] Neutral and acidic polypeptides containing photoisomerizable azo aromatic moieties have been investigated by three groups.[5–7] More recently, we have studied the light-induced properties of cationic amino acid lysine,[1] arginine oligopeptide[8] and lysine polypeptides containing azobenzene moieties.[9–13] The photochromic properties were reversible in covalently bonded systems[8,11–13] and irreversible in electrostatic interaction systems.[9,10] However, many unanswered questions still remain. The first difficulty in a study of such photochromic systems is their solubility, since azo aromatic peptides with high azo moieties are only sparingly soluble in common solvents. Secondly, the origin of the ellipticities in the 260–550 nm wavelength region, which is expected to involve the chiral coupling of the transition dipole moments of azo moieties, has not yet been solved clearly.

In this paper disubstituted azo aromatic L-lysine homologues (lysine, ornithine, diaminobutyric acid, and diaminopropionic acid) and their two antipodes (D-lysine and D-ornithine) have been investigated in order to further knowledge of photochromic changes in azo aromatic peptide systems, as well as to provide a clue as to the reasons for the improved solubility. The exciton chirality method was examined in order to explain how the azo aromatic chromophores under chiral environments interact with each other.

Experimental

Materials.—L-Lysine·HCl and L-ornithine·HCl were purchased from the Nippon Rikagakuyakuhin Co., Ltd. L-2,4-Diaminobutyric acid·2HCl, L-2,3-diaminopropionic acid·HCl, and *p*-phenylazobenzoyl chloride were purchased from the Tokyo Chemical Industries Co., Ltd. D-Lysine was purchased from the Kokusan Chemical Works Ltd. D-Ornithine HCl and the azo aromatic pentapeptide, 4-phenylazobenzyloxycarbonyl-L-prolyl-L-leucylglycyl-L-prolyl-D-arginine, were purchased from the Sigma Chemical Co., Ltd. Poly[ε-*N*-(phenylazobenzoyl)-L-lysine] (PPABLL) has been synthesized previously.[12]

Synthesis.—General procedure. To a cold solution of the lysine homologues (di- or monohydrochloride, 1 mmol) in NaOH (1 mol dm^{-3}, 1.1 cm^3) and dioxane (1.1 cm^3) were added *p*-phenylazobenzoyl chloride (1.1 mol) in dioxane (3 cm^3), and the mixtures were stirred for 2 h at 5 °C and overnight at room temperature. The mixture was acidified to Congo red with HCl (1 mol dm^{-3}) and then water (25 cm^3) was added. The resulting precipitate was filtered and recrystallized from dioxane and hexane. The analytical data are listed in Table 1.

Methods.—The absorption spectra and c.d. spectra were measured with a Jasco UVIDEC-1 spectrometer and a CD J-40A spectrometer, respectively. The spectroscopic data were expressed in terms of mean residue ellipticity [θ] (deg cm^2 $dmol^{-1}$) and molar extinction coefficient ε (dm^3 mol^{-1} cm^{-1}).

Irradiation of the sample solutions was carried out at 25 °C with a mercury lamp (400 W), filtered with narrow-band interference filters from Toshiba Ltd. The light intensity was determined by chemical actinometry using potassium ferrioxalate[14] to be 1.8×10^{19} photons cm^{-2} s^{-1} at 360 nm and 1.3×10^{19} photons cm^{-2} s^{-1} at 460 nm.

The dipole moment of 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP) was observed by the solution method using benzene as a solvent. The dielectric constant was measured by the heterodyne beat method at 3 MHz and the calculation of the dipole moment was carried out by the Halverstadt–Kumler equation. The details of the measurement of the dipole moment was the same as that used in a previous paper by one of the authors (T. S.).[15]

Table 1. Di- and mono-phenylazobenzoyl amino acids.

Amino acid[a]	Yield (%)	M.p./°C	$[\alpha]^b$	Anal. Found % C	Found % H	Found % N	Calc. % C	Calc. % H	Calc. % N
DPAB-L-Lys	73	227	−128°	68.45	5.32	14.94	68.31	5.37	14.94
DPAB-D-Lys	82	229	132°	68.60	5.32	15.05	68.31	5.37	14.94
DPAB-L-Orn	80	245	−20°	67.75	5.12	15.27	67.87	5.14	15.32
DPAB-D-Orn	81	244	20°	67.58	4.99	15.23	67.87	5.14	15.32
DPAB-L-DBA	88	240	−56°	67.60	4.86	15.92	67.40	4.90	15.72
DPAB-L-DPA	71	239	−128°	66.70	4.48	16.04	66.91	4.65	16.15
MPAB-L-Lys(Z)	92	151	16°	66.50	5.65	11.79	66.38	5.78	11.47
Boc-L-Lys(MPAB)	88	141	7°[c]	63.28	6.54	12.21	63.42	6.65	12.33
L-Lys(MPAB)·HCl	68	250	8°[d]	58.37	5.86	14.14	58.38	5.93	14.33

[a] Abbreviations used: DPAB, diphenylazobenzoyl; MPAB, monophenylazobenzoyl; Z, benzyloxycarbonyl; Boc, *t*-butoxycarbonyl. [b] $c = 0.25$ in dioxane at 25 °C. [c] $c = 1$ in dioxane at 25 °C. [d] $c = 0.25$ in methanol at 25 °C.

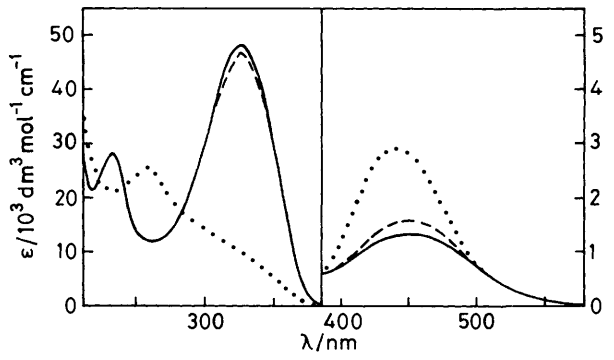


Figure 1. Absorption spectra of DPAB-L-Lys in *p*-dioxane at 25 °C; before irradiation (*trans*,——); after irradiation at 360 nm for 10 min (*cis*, · · · ·); after reirradiation at 460 nm for 10 min (photostationary state, – – – –).

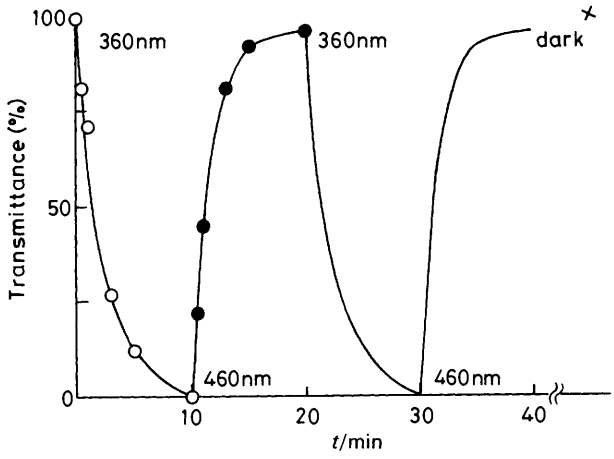
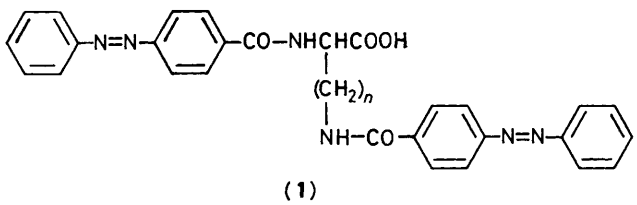


Figure 2. Kinetics of the photochemical isomerization of DPAB-L-Lys in *p*-dioxane: irradiation at 360 nm (○); irradiation at 460 nm (●); dark adaptation (×).

Results and Discussion

Azo Aromatic Amino Acids.—The origin of the ellipticity of the photochromic azo aromatic polypeptides reported to date is still obscure.[5–7] The reason is clear, *i.e.* the backbone conformational fluctuation and the geometrical change in the side chains occur together upon irradiation with light. In order to exclude the backbone contribution to the ellipticity, we used the diphenylazobenzoyl (DPAB) lysine homologues (**1**). The



(**1**)

n
1 Diaminopropionic acid
2 Diaminobutyric acid
3 Ornithine
4 Lysine

related monophenylazobenzoylated (MPAB) lysine derivatives α-Boc-ε-MPAB-L-Lys, α-MPAB-ε-*Z*-L-Lys, and ε-MPAB-L-Lys·HCl were prepared in order to measure the ellipticity.

Photoconversion.—Figure 1 shows the changes in the absorption spectra of DPAB-Lys in *p*-dioxane upon irradiation. Before irradiation (*trans*, in the dark), DPAB-L-Lys exhibits absorption bands at 217, 232, 258, 327, and 440 nm. The wavelength bands exhibit photochromism when the *trans* conformer converts to *cis* on irradiation at 360 nm (u.v.), whereas on re-irradiation of the solution at 460 nm (visible) the *cis* conformer returns mostly to *trans*. Here the absorption bands at *ca.* 330 and 430 nm are associated with the π–π^* and n–π^* transitions of the azo aromatic moieties.[6] The kinetic data for photoconversion of DPAB-L-Lys on irradiation at u.v. and visible wavelengths shows that the conversion is almost reversible (Figure 2). Though no fundamental spectroscopic change due to the *trans* $\rightleftharpoons$ *cis* photoisomerization was observed either between the DPAB- and MPAB-lysine derivatives, or among the DPAB-homologues with a different methylene number in the side chain, the rate of photoconversion of the DPAB-derivatives was faster than the MPAB derivatives. Table 2 summarizes the absorption results of DPAB- and DMAB-amino acids in solvents at 25 °C.

Solubility Change.—The critical solubilities of *trans*-DPAB-L-Lys at 25 °C are 3.8×10^{-4} mol dm^{-3} in a *p*-dioxane–water mixture (1:1.1, v/v) and 2.3×10^{-4} mol dm^{-3} in acetonitrile, while those of the *cis* isomer are 1.6×10^{-3} mol dm^{-3} in a *p*-dioxane–water mixture (1:1.1, v/v) and 9.8×10^{-4} mol dm^{-3} in acetonitrile. The *cis* isomer is 4.3 times more soluble in solvents than its *trans* isomer.

Since two conformers of azobenzene have two different dipole moments (μ) of 0.5 D (*trans*) and 3.1 D (*cis*),[16] before irradiation we made the DPAB-L-Lys solutions turbid by mixing low and high dipole-moment solvents or by cooling a heated solution

Table 2. Molar extinction coefficients of DPAB-L-Lys homologues before and after irradiation at 360 nm for 20 min in dioxane.

	ε (dm³ mol⁻¹ cm⁻¹)				
Sample	217 nm	232 nm	258 nm	327 nm	440 nm
DPAB-L-Lys[a]	21 400(t)[b]	28 300(p)	12 000(t)	48 600(p)	1 550(p)
	26 300	21 100(t)	25 600(p)	10 000	2 920(p)
DPAB-L-Orn	21 000(t)	27 700(p)	11 800(t)	48 900(p)	1 400(p)
	25 600	21 000(t)	25 400(t)	9 360	2 800(p)
DPAB-L-DBA	20 200(t)	27 400(p)	11 000(t)[c]	49 900(p)	1 240(p)
	25 300	21 000(t)	24 900(p)[c]	9 300	2 720(p)
DPAB-L-DPA	19 100(t)	27 000(p)	9 120(t)[c]	51 400(p)	1 120(p)
	24 600	20 500(t)	24 200(p)[c]	9 200	2 760(p)
MPAB-L-Lys(Z)	13 800(t)[d]	12 400(p)	6 360(t)	28 900(p)	680(p)
	13 200[d]	12 000(t)	14 700(p)	5 440	1 520(p)
Boc-L-Lys(MPAB)	11 500(t)	14 900(p)	5 960(t)[e]	25 700(p)[f]	920(p)
	13 900	11 100(t)	13 400(p)[e]	5 000[f]	1 560(p)
L-Lys-(MPAB)·HCl[g]	24 500(t)[h]	27 800(p)[i]	13 700(t)[e]	29 500(p)[j]	920(p)
	25 100[h]	22 100(t)[i]	24 200(p)[e]	12 000[j]	1 440(p)

[a] Upper row, *trans*, before irradiation; lower row, *cis*, after irradiation. [b] In parentheses: t, trough; p, peak. [c] 260 nm. [d] 222 nm. [e] 257 nm. [f] 328 nm. [g] In methanol. [h] 216 nm. [i] 230 nm. [j] 324 nm. Abbreviations, see Table 1.

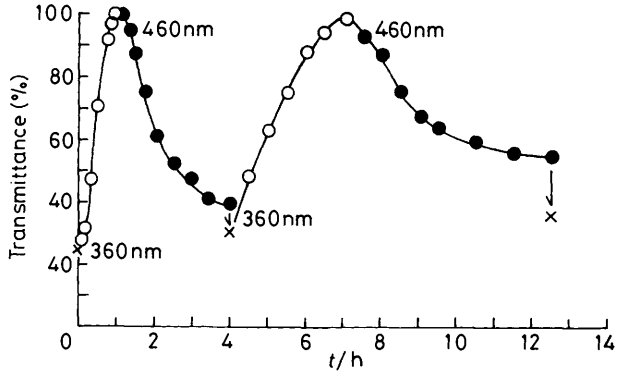


Figure 3. Solubility change of DPAB-L-Lys on irradiation at different wavelengths in *p*-dioxane–water (1:1.1, v/v) at 25 °C: dark adaptation (×). Concentration, 4.8 × 10^{-4} mol dm^{-3}. Transmittance at 650 nm.

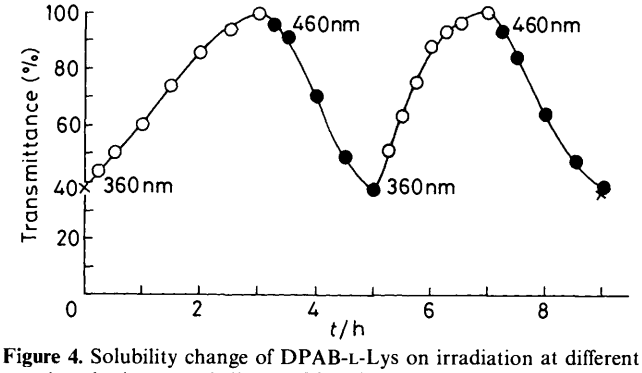


Figure 4. Solubility change of DPAB-L-Lys on irradiation at different wavelengths in acetonitrile at 25 °C: dark adaptation (×). Concentration, 5 × 10^{-4} mol dm^{-3}. Transmittance at 650 nm.

to a temperature between the critical solubilities of the *trans* and *cis* isomers. For example, to a solution of *trans* DPAB-L-Lys in 1 cm^3 of *p*-dioxane (μ, 0 D),[17] was added 1–1.1 cm^3 of water (μ, 1.9 D) until the mixture became turbid. The turbid mixture became clear on irradiation at 360 nm for 1 h, corresponding to photoconversion to the *cis* isomer. On re-irradiation at 460 nm the clear solution became turbid again, as shown in Figure 3.

Figure 4 shows the reversible solubility change of DPAB-L-

* 1 D = 3.335 64 × 10^{-30} C m.

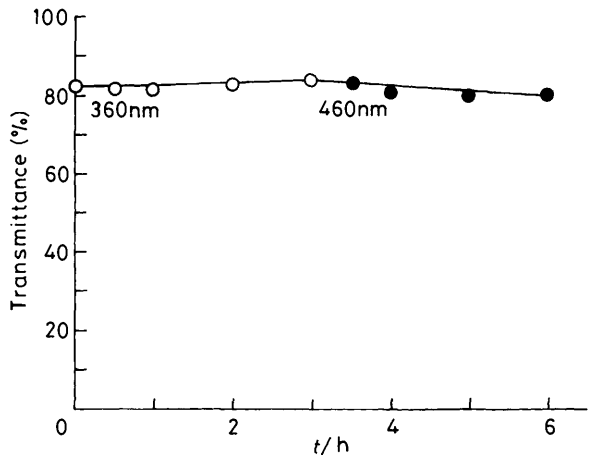


Figure 5. Solubility change of DPAB-L-Lys on irradiation at different wavelengths in *p*-dioxane–hexane (1:3, v/v). Concentration, 2.5 × 10^{-4} mol dm^{-3}. Transmittance at 650 nm.

Lys in acetonitrile (μ, 3.8 D). In acetone (μ, 2.9 D) and an acetone–hexane (μ, 0.09 D) mixed solvent the DPAB-L-Lys photoresponded as for acetonitrile solvent. As shown in Figure 5, on the other hand, the solubility of DPAB-L-Lys changes little in a dioxane (0 D) *–hexane (0.09 D) mixed solvent (1:3, v/v) on irradiation at 360 nm and 460 nm for 6 h. This suggests that the dipole moments of both solvent and azo aromatic moiety participate in the solubilizing factor of the system. The D-antipode, DPAB-D-Lys, exhibited the same solubility behaviour on irradiation as DPAB-L-Lys. Although the photoinduced solubility changes due to photoisomerization of the azo aromatic moieties in polar solvents are reversible, the time taken to complete the first and second cycles took 4 and 8 h, respectively, in a *p*-dioxane–water mixed solvent [*c.f.* 5 and 4 h in acetonitrile (Figures 3 and 4)]. These times seem to depend on the crystal form and size of crystal precipitated. In fact, when an ultrasonic vibrator was used, the photoinduced solubilizing and precipitating solubility change in a solvent exhibited an identical repeating cycle. Moreover, though not so marked, the dark adaptation after irradiation at 460 nm further decreased the transmittance of the system.

trans-Azo aromatic polypeptide, PPABLL, is only soluble in HFIP. The solubility change of PPABLL in a HFIP (μ, 2.5 D)–

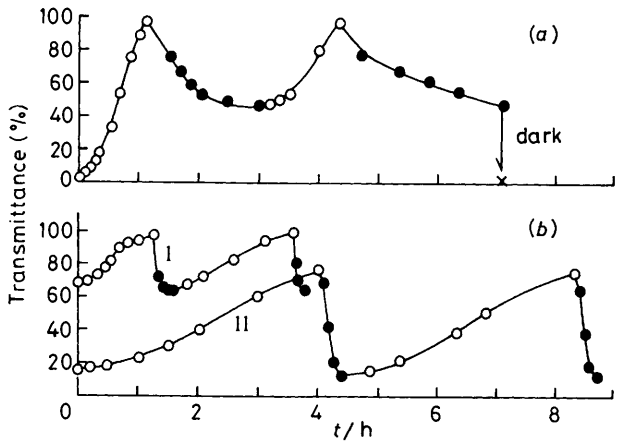


Figure 6. Solubility change of DPAB-L-Lys (*a*) and PPABLL (*b*) on irradiation at different wavelengths in HFIP–water (100:15, v/v) at 25 °C; irradiation at 360 nm (○) and 460 nm (●). Concentrations, 5.2×10^{-3} mol dm^{-3}, (*a*); 8.3×10^{-4} mol residue dm^{-3}, (*b*)-I; 3.5×10^{-3} mol residue dm^{-3}, (*b*)-II. Transmittance at 650 nm.

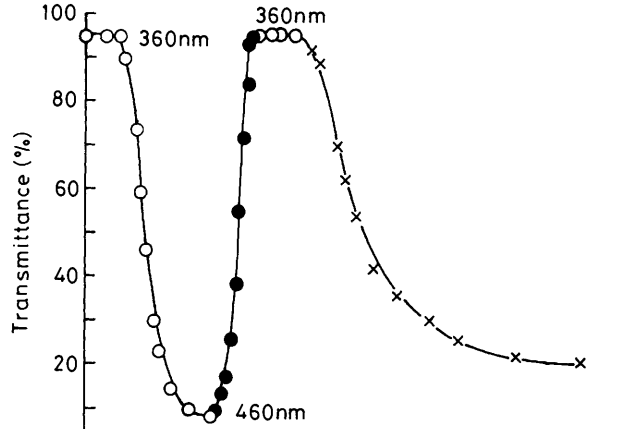


Figure 7. Solubility change of azo aromatic pentapeptide on irradiation at different wavelengths in *p*-dioxane–CCl_4 (5:3, v/v) at 25 °C; irradiation at 360 nm (○) and at 460 nm (●); spontaneous crystallization without light (×). Concentration, 6.6×10^{-4} mol dm^{-3}. Transmittance at 650 nm.

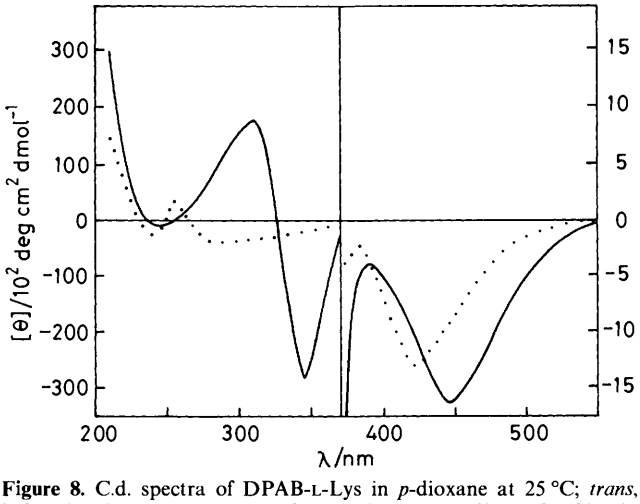


Figure 8. C.d. spectra of DPAB-L-Lys in *p*-dioxane at 25 °C; *trans*, before irradiation (——); *cis*, after irradiation at 360 nm for 20 min (· · · ·).

water (100:15, v/v) mixed solvent at 25 °C is depicted in Figure 6(*b*). The solubility changes on irradiation at 360 and 460 nm were dependent on the polypeptide concentration and were found to take 4 h (solubilizing) and 15 min (precipitating) at 3.5×10^{-3} mol residue dm^{-3}, respectively; this is much slower than the results for DPAB-L-Lys shown in Figures 6(*a*). In this connection Irie *et al.*[18–20] recently investigated the photostimulated reversible solubility change of aggregated random-coiled polystyrene and α-helical polyglutamic acid containing azobenzene. The reported time required to complete one cycle, first solubilizing and then precipitating, was 6 min for azo aromatic polystyrene[18,19] and at least 1 h for azo aromatic polyglutamic acid.[20] In any event, the azo aromatic amino acids described here exhibit the longest response time for their solubility change in polar solvents. The reason for the rapid solubility change in polymer systems may be attributed to their low azo aromatic contents.

A reverse photo-induced precipitating (u.v.)-solubilizing (visible) effect is depicted in Figure 7. Azo aromatic pentapeptide is very soluble in water and various organic solvents. A clear solution of the peptide in *p*-dioxane–CCl_4 (μ, 0 D) (5:3 v/v) became cloudy after irradiation at 360 nm for 5 min. Irradiation was then stopped but spontaneous crystallization continued for a further 30 min (× in Figure), while after further irradiation at 360 nm the precipitation became much faster. On irradiation at 460 nm, the turbid suspension soon became clear.

Figure 8 shows the c.d. spectra of DPAB-L-Lys in dioxane at 5×10^{-4} mol dm^{-3}. Before irradiation, the DPAB-L-Lys in dioxane exhibited four dichroic bands, at 445 nm with $[\theta]_{445} = -1\,650$, at 345 nm with $[\theta]_{345} = -28\,600$, at 310 nm with $[\theta]_{310} = 18\,000$, and at 207 nm with $[\theta]_{207} = 35\,400$. The DPAB-D-Lys exhibited ellipticities of $[\theta]_{445} = 1\,500$, $[\theta]_{345} = 28\,300$, $[\theta]_{306-310} = -16\,800$, and $[\theta]_{207} = -32\,200$, and was of almost opposite sign to the DPAB-L-Lys. The DPAB-L-Lys exhibited the same dichroic bands with somewhat lower ellipticities in ethanol. Light produces a photochromism in the c.d. spectra of DPAB-L- and D-Lys in dioxane (and ethanol). On irradiation at 360 nm for 60 min, the negative dichroic band of DPAB-L-Lys at 445 nm due to the n–π^* electronic transition decreased its ellipticity in magnitude ($[\theta]_{422} = -1\,320$), and two dichroic bands at 345 nm and 310 nm, due to the long and short axis transitions, changed and decreased their ellipticities. The same photoinduced behaviour (with opposite sign) were observed in DPAB-D-Lys.

The absorption and c.d. bands at *ca.* 260–390 nm were examined by the exciton chirality method,[21–24] where Δε is the

$$\Delta\varepsilon(\sigma) = \frac{2\sqrt{\pi}\sigma_0^2}{2.296 \times 10^{-39}\Delta\sigma^2}\left(\frac{\sigma_0 - \sigma}{\Delta\sigma}\right)\exp\left[-\left(\frac{\sigma_0 - \sigma}{\Delta\sigma}\right)^2\right] \cdot R_{ij}(\mu_{ioa} \cdot \mu_{joa})V_{ij} \quad (1)$$

c.d. value, σ_0 and $\Delta\sigma$ are the excitation wave numbers of the isolated non-interacting chromophore and the standard deviation of the Gaussian distribution, R_{ij} and V_{ij} are the interchromophoric distance vectors from i to j and the transition dipole interaction energy between chromophores i and j, and μ_{ioa} and μ_{joa} are the electric transition moment vectors of i and j. The second term in equation (1) has been reported as both quantitative and qualitative definitions of exciton chirality for a series of steroidal glycol bis(benzoates).[24] The calculated curve, calculated taking $\Delta\sigma_2$ 2 200 cm^{-1} [rather than a standard derivation $(\Delta\sigma_1 + \Delta\sigma_2)/2$] and using a microcomputer (NEC PC-9801) in the corresponding wavelength region is depicted in Figure 9, together with the observed absorption spectrum. Thus the ellipticity in the 260–390 nm region can be assigned to the coupling of the long-axis

Table 3. Molar ellipticities of DPAB-L-Lys homologues before (*trans*) and after (*cis*) irradiation at 360 nm for 20 min in dioxane.[a]

Sample	Conformer	[θ] deg cm^2 dmol^{-1} (nm)		
DPAB-L-Lys	*trans*	−1 650 (445)	−28 600 (345)	18 000 (310)
	cis	−1 320 (422)	−3 730 (280)	3 650 (256)
DPAB-D-Lys	*trans*	1 500 (445)	28 300 (345)	−16 800 (306)
	cis	1 280 (422)	2 400 (280)	−6 200 (256)
DPAB-L-Orn	*trans*	−180 (435)	−16 500 (345)	8 800 (304)
	cis	−290 (420)	−2 900 (283)	6 100 (255)
DPAB-D-Orn	*trans*	160 (435)	15 600 (344)	−9 100 (304)
	cis	270 (420)	2 600 (283)	−7 200 (255)
DPAB-L-DBA	*trans*	−380 (435)	−25 800 (344)	13 700 (307)
	cis	−1 300 (418)	−4 900 (340)	−2 300 (280)
DPAB-L-DPA	*trans*	−710 (445)	−38 000 (343)	18 200 (304)
	cis	300 (420)	−9 600 (343)	−1 840 (280)
MPAB-L-Lys(Z)	*trans*	160 (460)	−1 000 (325)	2 000 (280)
	cis	300 (450)	2 780 (258)	−2 200 (235)
Boc-L-Lys(MPAB)	*trans*	220 (450)		
	cis	220 (450)		

[a] Abbreviations, see Table 1.

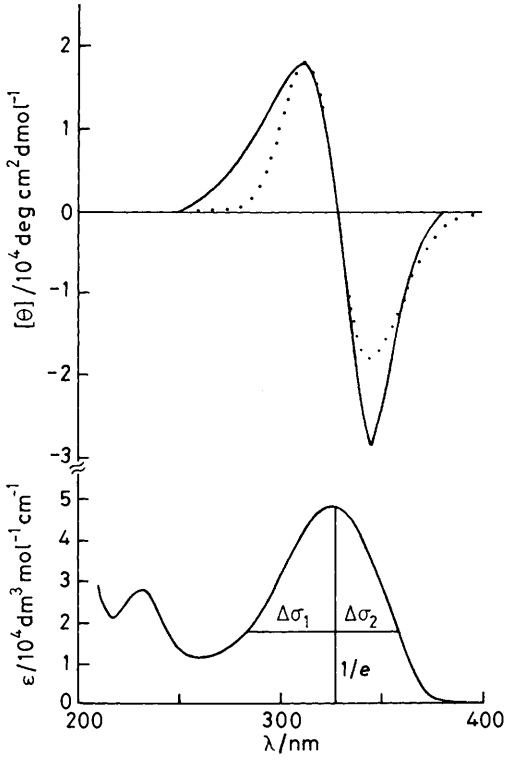


Figure 9. C.d. (upper) and absorption spectra (lower) of *trans*-DPAB-L-Lys in *p*-dioxane; observed c.d. (——); calculated from the equation (1) (· · · ·). Details, see text.

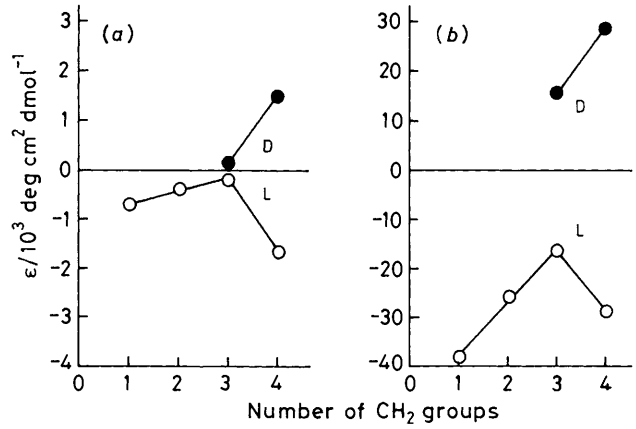


Figure 10. Molar ellipticity values of the DPAB-Lys homologues in *p*-dioxane as a function of the number of methylene groups; azobenzene chromophore *n*–π* (*a*) and π–π* (*b*) transition region; D and L mean D- and L-antipodes.

transition dipole moment of *trans* azo aromatic moieties and the chirality between two transition dipole moments is negative. By analogy with the case of rotational strength, dipole strength can be estimated from the observed absorption spectra.[24] Integration over the *trans* π–π* absorption area from 260–390 nm gives the dipole strength value of 9.4 × 10^{-35} cgs unit.* From this value, an electric transition moment μ of 9.7 D and an electric transition dipole moment of 2.0 Å were obtained.

Table 3 summarizes the c.d. results of photochromism in the DPAB-lysine series. Figure 10 exhibits the relationship between the ellipticities at 435–445 and 345 nm and the number of methylene groups in the side chain. When an azo aromatic polypeptide has a longer side chain length (n = 1–3), the ellipticities due to the π–π* and *n*–π* transitions exhibited smaller magnitudes, whereas the azo aromatic lysine with the longest n (= 4) exhibits a larger ellipticity than expected. This fact suggests two possibilities which enhance the coupling of chromophores under the asymmetric carbon: (*i*) four aliphatic methylene groups interact hydrophobically to promote a closer stacking of azo aromatic chromophores, and/or (*ii*) an azo aromatic chromophore at the ω-amino group of a longer side chain (than n = 4) could fold back to come closer to the asymmetric carbon, which could interact more strongly with the azo chromophore at the α-amino group. This latter possibility has been proposed by us previously[25] and the present results may be additional support for this. Here the even–odd rule of hydrocarbon chain number was not observed in the ellipticities. Besides, contrary to expectation, two MPAB-L-lysine derivatives in organic solvents such as dioxane and ethanol, and MPAB-L-lysine hydrochloride in water and methanol exhibited small but definite ellipticities in the 300—450 nm wavelength region. One example is depicted in Figure 11. This means that a contribution from the chiral interaction between the symmetric carbon and mono azo aromatic chromophore cannot be ignored in the quantitative evaluation of ellipticity.

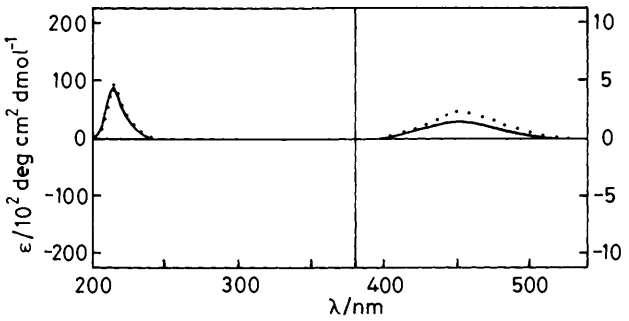


Figure 11. C.d. spectra of α-Boc-ε-MPAB-L-Lys in *p*-dioxane at 25 °C; *trans* (——); *cis* (· · · ·).

To summarize, the possibility of improving the solubility of dye containing polypeptide systems has been proposed from the standpoint of the dipole moments of both dye and solvent. The origin of chiral photochromism has been examined from dipole coupling theory. The coupling of the asymmetric C_α carbon and azo aromatic chromophore participates in the ellipticity to a small extent.

Acknowledgements

The present work was supported by a Grant-in-Aid for Scientific Research (No. 61490014) from the Ministry of Education, Science and Culture.

References

1 Part 6, H. Yamamato and A. Nishida, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 2201.
2 R. Lovrien, P. Pecheck, and W. Tisel, *J. Am. Chem. Soc.*, 974, **96** 2441.
3 R. Van der Veen, R. Houguest, and W. Prins, *Photochem. Photobiol.*, 1974, **19**, 97.
4 J. C. Lagarias and H. Rapoport, *J. Am. Chem. Soc.*, 1980, **102**, 4821
5 M. Goodman and K. Kossoy, *J. Am. Chem. Soc.*, 1966, **88**, 5010.
6 A. Ueno, K. Takahashi, J. Anzai, and T. Osa, *J. Am. Chem. Soc.*, 1981, **103**, 6410.
7 O. Pieroni, J. L. Houben, A. Fissi, P. Constantino, and F. Ciardelli, *J. Am. Chem. Soc.*, 1980, **102**, 5913.
8 H. Yamamoto and A. Noshida, *Photochem. Photobiol.*, 1988, **42**, 149.
9 H. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1985, **58**, 2439.
10 H. Yamamoto, A. Nishida, and K. Inouye, *Polym. Photochem.*, 1986, **7**, 349.
11 H. Yamamoto and A. Nishida, *Macromolecules*, 1986, **19**, 943.
12 H. Yamamoto, *Macromolecules*, 1986, **19**, 2472.
13 H. Yamamoto, Y. Miyagi, A. Nishida, T. Takagishi, and S. Shima, *J. Photochem.*, 1987, **39**, 343.
14 J. G. Calvert and J. N. Pitts Jr., in 'Photochemistry,' Wiley, New York, 1966, p. 783.
15 T. Shimozawa, *Bull. Chem. Soc. Jpn.*, 1955, **28**, 389.
16 D. W. Bullock, C. N. Cumper, and I. Vogel, *J. Chem. Soc.*, 1965, 5316.
17 The Dipole moments of the organic solvents, (except HFIP) were taken from 'Handbook of Chemistry and Physics,' ed. C. D. Hodgman, Chemical Rubber Pub. Co., Cleveland, 1961, pp. 2569–2576.
18 M. Irie and H. Tanaka, *Macromolecules*, 1983, **16**, 210.
19 M. Irie and W. Schnabel, *Macromolecules*, 1985, **18**, 394.
20 M. Irie and O. Pieroni, *Polym. Prepr. Jpn.*, 1987, **36**, 2814.
21 I. Tinoco Jr., *Adv. Chem. Phys.*, 1962, **4**, 113.
22 P. Crabbe, in 'ORD and CD in Chemistry and Biochemistry,' Academic Press, New York, 1972.
23 N. Harada, S. L. Chen, and K. Nakanishi, *J. Am. Chem. Soc.*, 1975, **97**, 5345.
24 K. Nakanishi and N. Harada, in 'Circular Dichroic Spectroscopy—Exciton Coupling in Organic Stereochemistry,' University Science Book, Mill Valley, California, 1983.
25 H. Yamamoto and C. Hano, *Kobunshi Ronbunshu*, 1983, **40**, 405.

Received 1*st November* 1988; *Paper* 8/04352C