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Optical Activity of Crystalline Glutamic Acids

T. Asahi,* H. Utsumi, Y. Itagaki, I. Kagomiya and J. Kobayashi

Kagami Memorial Laboratory for Material Science and Technology, Waseda University, 2-8-26 Nishi-Waseda, Shinjuku-ku, Tokyo 169, Japan

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Abstract

As the first study on gyro-optical properties of amino acids, temperature dependences of the gyration tensor components of L- and D-glutamic acids were measured by using the HAUP (high-accuracy universal polarimeter). It was confirmed that the corresponding tensor components of the two enantiomers are the same in magnitude but opposite in sign. It is proposed that $r = (\rho_C^0 - \rho_S^0)/\rho_C^0$ be defined as the 'chirality index', where ρ_C^0 and ρ_S^0 designate rotatory powers per molecule in a crystal and in a dissolved state in liquid, respectively. It represents a measure of structural contribution of optical activity (OA) in a crystal. This value is 0.992 in glutamic acids.

1. Introduction

Optical activity (OA) has played a very important role in the progress of chemistry. However, practical measurements of the OA of compounds were mostly made in their liquid state or, only in favourable cases, along the optic axes in the solid state. OA takes place when some electrons are displaced along chiral paths by an applied electric field. Such a condition is realized when there are vicinal interactions between directionally oriented molecules. Therefore, it is possible that even if molecules are optically inactive in the liquid state they become optically active in a crystalline state because of additional constraints. A typical example of this case is α-quartz (Kauzmann & Eyring, 1941). Thus, OA is expected to be one of the most effective tools for looking at the crystal structure from the specific viewpoint of chirality.

However, birefringence existing in crystals, usually 10^3 times larger than OA, has prevented the measurements of OA since the discovery of OA (Arago, 1811).

We developed a high-accuracy universal polarimeter, HAUP (Kobayashi & Uesu, 1983; Kobayashi, Kumomi & Saito, 1986; Kobayashi, Asahi, Takahashi & Glazer, 1988), which enabled us to measure simultaneously gyration G, birefringence Δn and rotation angle Ψ of the indicatrix of any crystal. It appeared interesting to study the OA of amino acids that make up various proteins by using the HAUP method since, to our knowledge, there have been no papers reporting the OA of any crystals of amino acids. For this reason, we studied the OA of L- and D-glutamic acids (GA) as a first step to clarify the OA of amino acids. Each GA has two crystal polymorphs, α (Bernal, 1931) and β (Hirokawa, 1955) forms. Here, we selected the β-form crystals, which are more stable than the α form for slow crystallization from aqueous solutions (Sakata, 1961, 1962).

2. Measurements

The specimens of the β form of L- and D-GA were crystallized by the slow evaporation of saturated aqueous solutions at 303.7 K. The lattice constants of L-GA were determined by using Weissenberg photographs: $a = 5.16(2)$ [5.17], $b = 17.33(2)$ [17.34] and $c = 6.97(2)$ [6.95] Å at 298 K. They coincide with the values [in square brackets] given by Hirokawa (1955). The extinction rules for the X-ray reflections found in the photographs were consistent with those described by Hirokawa (1955). Therefore, we identified the space group of our GA specimens to be D_2^4-$P2_12_12_1$ according to Hirokawa's (1955) result.

We prepared six specimens, $(001)_L$, $(010)_L$, $(100)_L$, $(001)_D$, $(010)_D$ and $(100)_D$ plates of L- and D-GA. We determined first the optical orientation of the crystal using optical conoscopic and compensation methods on the $(001)_L$ plate. The results are that the crystallographic a, b and c axes are the optical Y, Z and X axes, respectively.

The polished specimens with dimensions indicated in Table 1 were subjected to HAUP measurements. Each specimen was placed in a vacuum chamber and held at various temperatures between 390 and 110 K within an accuracy of ±0.02 K. The light source was an He–Ne laser with a wavelength of 6328 Å. As the processes of determination of gyration and birefringence are described in previous papers (Kobayashi & Uesu, 1983; Kobayashi, Kumomi & Saito, 1986; Kobayashi, Asahi, Takahashi & Glazer, 1988), the descriptions of the present experiment are omitted. For the determination of the systematic error γ, our method (Kobayashi, Asahi, Takahashi & Glazer, 1988) was adopted by using optically inactive $LiNbO_3$ as the standard crystal, while

Table 1. *Dimensions and systematic errors for the specimens used in the present experiment*

	Dimensions		Systematic errors	
Specimen	Area (mm^2)	Thickness (mm)	γ ($\times 10^{-4}$)	$\delta\Upsilon$($\times 10^{-4}$)
$(100)_L$ plate	0.325 × 1.130	0.118	−12.3	−2.0
$(010)_L$ plate	3.470 × 1.250	0.051	−14.4	1.5
$(001)_L$ plate	0.380 × 3.250	0.140	−10.6	5.0
$(100)_D$ plate	0.255 × 0.955	0.179	3.5	5.5
$(010)_D$ plate	4.250 × 1.500	0.073	14.4	−3.7
$(001)_D$ plate	0.420 × 3.800	0.261	16.4	4.6

the other method for determining γ was suggested by Moxon & Renshaw (1990).

As a measure of the quality of the present optical system, the extinction ratio, *i.e.* the ratio of the intensity of the emergent light from the crossed Nicols system with respect to that of the incident light, reached 6×10^{-9}. This condition enabled us to determine the extinction positions of the specimen by rotating the crossed Nicols at 11 intervals within a small range of ±0.04°. We successfully determined the systematic errors of each specimen and they are also shown in Table 1. The temperature dependence of the gyration tensors, g_{11}, g_{22}, g_{33}, of the L and D crystals is represented in Fig. 1(*a*), and that of the birefringences, Δn_a, Δn_b and Δn_c, along each axis in Fig. 1(*b*).

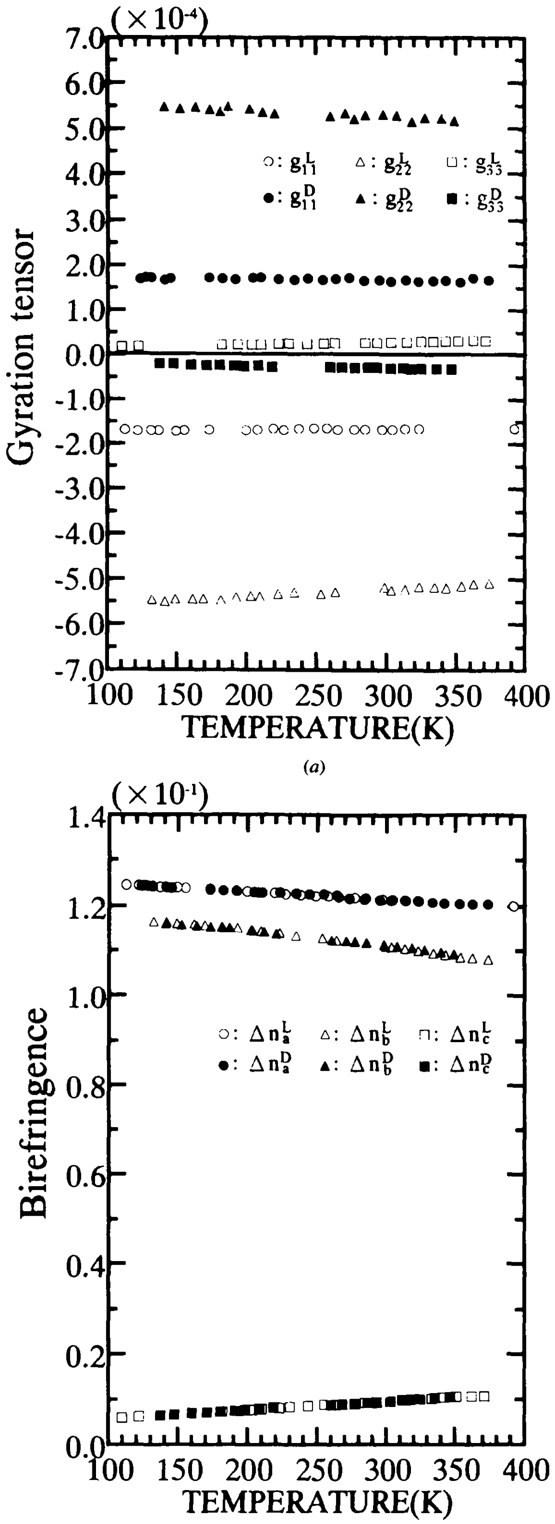
It has been clearly confirmed that the corresponding gyration tensor components of the different enantiomers are almost the same in magnitude but opposite in sign. On the contrary, the birefringences of the two enantiomers coincide perfectly. From the gyration tensor components of L-GA, rotatory powers ρ_a, ρ_b and ρ_c along the *a*, *b* and *c* axes are calculated as $\rho_a = -308$, $\rho_b = -978$ and $\rho_c = 54° \text{cm}^{-1}$ and are compared in Table 2 with data from other crystals. ρ_c is smaller than ρ_a and ρ_b with different sign. The gyration surface (Shubnikov, 1960) of L-GA is schematically depicted in Fig. 2(*a*). It consists of black and white ovoids; the former corresponds to the gyrations with negative sign, the latter (exaggeratedly drawn) those with positive sign. Sections of the gyration surface with (001), (100) and (010) planes are depicted in Figs. 2(*b*), (*c*) and (*d*).

3. Discussion

The trajectory of the directions of the light beam where the gyration *G* vanishes was calculated. *G* of GA is represented by the components of the wave vector s ($s_1 = \cos\theta_1$, $s_2 = \cos\theta_2$, $s_3 = \cos\theta_3$) of incident light as follows:

$$\begin{aligned} G &= g_{11}s_1^2 + g_{22}s_2^2 + g_{33}s_3^2 \\ &= (g_{11} - g_{33})s_1^2 + (g_{22} - g_{33})s_2^2 + g_{33}. \end{aligned} \quad (1)$$

Then the trajectory for $G = 0$ is given by



(*a*)

(*b*)

Fig. 1. Temperature dependences of (*a*) the gyration tensor components and (*b*) the birefringences of L- and D-glutamic acids along *a*, *b* and *c* axes. Plots of the L acid are denoted by open symbols and those of the D acid by full ones.

Table 2. *Optical rotatory powers of crystals*

Crystal	λ (Å)	T (K)	ρ (° cm^{-1})
$AgGaS_2$	4850		9500[a]
$Ca_2Sr(C_2H_5COO)_6$	5890	293	42[b]
α-HgS	6328		−3200[c]
$Bi_{12}SiO_2$	6500		−205[d]
α-$LiIO_3$	6328		−867[e]
$[N(CH_3)_4]_2ZnCl_4$	6328	292	0.2[f]
α-SiO_2	6328	293	251[g]
TeO_2	6328		870[h]
Hg_2I_2	6328		2320[h]
$NaKC_4H_4O_6\cdot 4H_2O$	6328	298	−9.6[i]
$BaMnF_4$	6328	133	57[j]
$(C_3H_7NH_3)_2MnCl_4$	6328	355	22[k]
$(NH_2CH_2CO_2H)_3H_2SO_4$	6328	305	19[l]
Poly(L-lactic acid)	5145	298	−92000[m]
L-Glutamic acid (ρ_a)	6328	293	−308
L-Glutamic acid (ρ_b)	6328	293	−978
L-Glutamic acid (ρ_c)	6328	293	54

References: (*a*) Hobden (1967); (*b*) Kobayashi, Bouillot & Kinoshita (1971); (*c*) Ayrault, Lefin, Langlois, Toudic & Palmier (1972); (*d*) Abrahams, Svensson & Tanguay (1979); (*e*) Stadnicka, Glazer & Moxon (1985); (*f*) Kobayashi, Saito, Takahashi & Kamiya (1993); (*g*) Kobayashi, Asahi, Takahashi & Glazer (1988); (*h*) McCarthy, Goutzoulis, Gottlieb & Singh (1987); (*i*) Kobayashi, Uchino & Asahi (1990); (*j*) Asahi, Tomizawa, Kobayashi & Kleemann (1992); (*k*) Saito & Kobayashi (1992); (*l*) Kobayashi, Uchino, Matsuyama & Saito (1991); (*m*) Kobayashi, Asahi, Ichiki, Oikawa, Suzuki, Watanabe, Fukada & Shikinami (1995).

$$[(g_{33} - g_{11})/g_{33}]s_1^2 + [(g_{33} - g_{22})/g_{33}]s_2^2 = 1. \quad (2)$$

As a special case, the sections of the trajectory with the (100) plane are two lines with $\theta_1 = \pi/2$ and $\theta_2 = \pm\cos^{-1}[g_{33}/(g_{33} - g_{22})]^{1/2} = \pm 76.7°$. The sections of the trajectory with the (010) plane are two lines with $\theta_1 = \pm\cos^{-1}[g_{33}/(g_{33} - g_{11})]^{1/2} = \pm 67.2°$ and $\theta_2 = \pi/2$.

It will be of interest to compare rotatory powers per GA molecule when it is contained in a crystal lattice and dispersed in a liquid solution. Let us now consider a fibrous aggregate of a crystal with a volume of 1 ml, which consists of crystallites in perfectly random orientations. The rotatory power of this assembly of the crystal, ρ_C, is expressed as

$$\rho_C = (\pi\bar{g}/\lambda\bar{n})(180/\pi) \times 10^5\,[° \,\mathrm{m}^{-1}\,\mathrm{l}^{-1}], \quad (3)$$

where $\bar{g}$ represents the averaged gyration tensor of the crystal. In the case of the orthorhombic system, $\bar{g} = \frac{1}{3}(|g_{11}| + |g_{22}| + |g_{33}|)$. $\bar{g}$ of GA can be calculated as 2.5×10^{-4}. Therefore, ρ_C of GA is estimated as 4.7×10^{7}° m^{-1} l^{-1}. On the other hand, the number of GA molecules contained in this assembly, N_C, is

$$N_C = (Z/abc) = 6.4 \times 10^{24}\,[\mathrm{l}^{-1}], \quad (4)$$

where $Z = 4$ (Hirokawa, 1955) is the number of molecules contained in a unit cell. Thus, the rotatory power per molecule in a crystal lattice, ρ_C^0, is given by

$$\rho_C^0 = \rho_C/N_C = 7.4 \times 10^{-18}\,[° \,\mathrm{m}^{-1}]. \quad (5)$$

Rotatory powers of GA in aqueous solutions were studied by Patterson & Brode (1943) and Katzin & Gulyas (1964). [*M*] varies considerably with the change of acidity of solutions. It is easy to calculate the rotatory power per molecule in an aqueous solution, ρ_S^0, when GA manifests maximum molecular rotation, *i.e.* [*M*] in the solvent with 2*M* HCl. In this case,

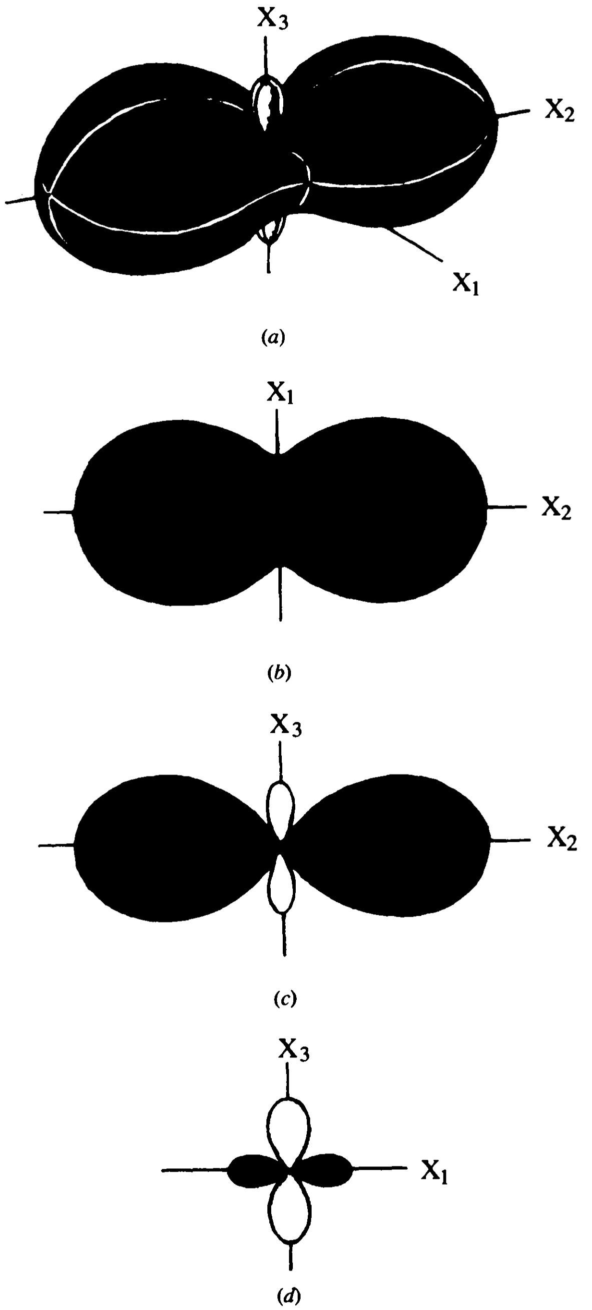


Fig. 2. Schematic representations of the gyration surface of L-glutamic acid: (*a*) birds-eye view; (*b*) section of the gyration surface with (001) plane; (*c*) section with (100) plane; (*d*) section with (010) plane.

$$\rho_S^0 = 10|[M]|/N_A = 6 \times 10^{-20}\,[^\circ\,\mathrm{m}^{-1}], \quad (6)$$

where N_A is Avogadro's number.

Here we define the following quantity as r:

$$r = (\rho_C^0 - \rho_S^0)/\rho_C^0 = 1 - \rho_s^0/\rho_C^0. \quad (7)$$

This is a measure of the structural contribution of the OA in a crystal and represents the severity of the restriction of the freedom of molecular orientation by forming a crystal lattice. It is evident that r of α-quartz is 1 as $\rho_S^0 = 0$. In the case of GA, it becomes 0.992. Thus, it has been found that the structural contribution of OA of GA is predominantly large. The availability of values of r for other crystals is extremely poor; another example, to our knowledge, being 0.9994 for poly(L-lactic acid), a typical helical polymer (Ichiki, Asahi & Kobayashi, 1996). r is an effective quantity for assessing the chiral nature of optically active crystals. Therefore, we propose to define it as the 'chirality index' of the crystal. The evaluation of r for various crystals has now become possible by using the HAUP method, and is especially promising for obtaining new insights into chiral properties of amino acid crystals.

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References

Abrahams, S. C., Svensson, C. & Tanguay, A. R. Jr (1979). *Solid State Commun.* **30**, 293-295.

Arago, F. (1811). *Mem. Cl. Sci. Math. Phys. Inst.* **12**, 93-134.

Asahi, T., Tomizawa, M., Kobayashi, J. & Kleemann, W. (1992). *Phys. Rev. B*, **45**, 1971-1987.

Ayrault, B., Lefin, F., Langlois, H., Toudic, Y. & Palmier, J. F. (1972). *Opt. Commun.* **5**, 239-243.

Bernal, J. D. (1931). *Z. Kristallogr.* **78**, 363-369.

Hirokawa, S. (1955). *Acta Cryst.* **8**, 637-641.

Hobden, M. V. (1967). *Nature (London)*, **216**, 678.

Ichiki, M., Asahi, T. & Kobayashi, J. (1996). *Phase Transit.* **56**, 67-78.

Katzin, L. I. & Gulyas, E. (1964). *J. Am. Chem. Soc.* **86**, 1655-1659.

Kauzmann, W. & Eyring, H. (1941). *J. Chem. Phys.* **9**, 41-53.

Kobayashi, J., Asahi, T., Ichiki, M., Oikawa, A., Suzuki, H., Watanabe, T., Fukada, E. & Shikinami, Y. (1995). *J. Appl. Phys.* **77**, 2957-2973.

Kobayashi, J., Asahi, T., Takahashi, S. & Glazer, A. M. (1988). *J. Appl. Cryst.* **21**, 479-484.

Kobayashi, J., Bouillot, J. & Kinoshita, K. (1971). *Phys. Status. Solidi B*, **47**, 619-628.

Kobayashi, J., Kumomi, H. & Saito, K. (1986). *J. Appl. Cryst.* **19**, 377-381.

Kobayashi, J., Saito, K., Takahashi, N. & Kamiya, I. (1993). *Phys. Rev. B*, **48**, 10038-10046.

Kobayashi, J., Uchino, K. & Asahi, T. (1990). *Phys. Rev. B*, **43**, 5706-5712.

Kobayashi, J., Uchino, K., Matsuyama, H. & Saito, K. (1991). *J. Appl. Phys.* **69**, 409-413.

Kobayashi, J. & Uesu, Y. (1983). *J. Appl. Cryst.* **16**, 204-211.

McCarthy, K. A., Goutzoulis, A. P., Gottlieb, M. & Singh, N. B. (1987). *Opt. Commun.* **64**, 157-159.

Moxon, J. R. L. & Renshaw, A. R. (1990). *J. Phys. Condens. Matter*, **2**, 6807-6836.

Patterson, J. W. & Brode, W. R. (1943). *Arch. Biochem.* **2**, 247-257.

Saito, K. & Kobayashi, J. (1992). *Phys. Rev. B*, **45**, 10264-10270.

Sakata, Y. (1961). *Agric. Biol. Chem.* **25**, 829-834, 835-837.

Sakata, Y. (1962). *Agric. Biol. Chem.* **26**, 355-361.

Shubnikov, A. V. (1960). *Principles of Optical Crystallography*, p. 128. New York: Consultant Bureau.

Stadnicka, K., Glazer, A. M. & Moxon, J. R. L. (1985). *J. Appl. Cryst.* **18**, 237-240.