

## Molecular polarizabilities of some amino acids 1. Glycine and L-alanine

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MS received 11 October 1980; revised 10 March 1981

**Abstract.** Atom-dipole interaction model has been used to calculate the molecular polarizabilities, refractive indices along the direction of principal polarizabilities of glycine and L-alanine and the molar optical rotation of L-alanine. The results of the calculation have been compared with experimentally observed data from Kerr effect and polarimetric measurements.

**Keywords.** Atom-dipole interaction; molar optical rotation; Kerr effect; molecular polarizability; amino acids.

### 1. Introduction

The study of conformation of biomolecules has been of much interest in recent years because of its role in understanding the biological activity. It has been studied using several techniques such as ORD, CD, IR, Raman scattering, etc. From a theoretical point of view conformational maps have proved very useful. Molecular polarizability is also one of the conformation-dependent property. A study of molecular polarizability is important not only for a quantitative interpretation of the Raman spectra but also for understanding the optical behaviour of biomolecules (Partington 1953, Kirkwood 1937 and Pitzer 1959). In the present paper we report a study of molecular polarizabilities on the two simplest amino acids, glycine and L-alanine.

### 2. Theory

There are various theoretical approaches (Lippincott and Stutman 1964; Lippincott *et al* 1966; Le Fevre and Narayana Rao 1954; Buckingham and Orr 1967; Applequist *et al* 1972) which have been used in the calculation of molecular polarizabilities but not all of them reflect the conformational dependence. For example, in the atomic polarization method (Le Fevre and Narayana Rao 1954), it would be reflected only to the extent that the various bonded force constants are conformation-dependent. No fragment-fragment interactions which stabilize the secondary structure are considered. The atom dipole interaction model (Applequist *et al* 1972) which considers various bonded and nonbonded interactions is the one which is conformation-dependent and it is used here. Briefly, in this approach, a molecule is regarded as

being made up of  $N$  isotropic-atoms with their polarizabilities centred at their nuclei which interact with each other by way of their induced dipoles. If the molecule is subjected to an external electric field, the effective total electric field at an atom in the molecule consists of this applied field plus the field due to induced dipoles in all other atoms of the molecule. The effective field at the atom induces a dipole moment in it and the vector sum of induced dipole moments in all atoms gives the total dipole moment induced in the molecule. If the polarizability tensor for  $i$ th atom be  $\alpha_i$ , the induced dipole moment  $\mu_i$ , a column vector at this atom is given as (Applequist *et al* 1972)

$$\mu_i = \alpha_i \left[ \mathbf{E}_i - \sum_{\substack{j=1 \\ j \neq i}}^N T_{ij} \mu_j \right], \quad (1)$$

where  $\mathbf{E}_i$ , a column vector is the applied electric field at  $i$ th atom and  $T_{ij}$  is the induced dipole-dipole interaction tensor whose matrix (Bottcher 1952) form is given as

$$T_{ij} = -\frac{3}{r^5} \begin{bmatrix} x^2 - r^2/3 & xy & xz \\ xy & y^2 - r^2/3 & yz \\ xz & yz & z^2 - r^2/3 \end{bmatrix}, \quad (2)$$

where  $r$  is the distance between  $i$ th and  $j$ th atom and  $x$ ,  $y$  and  $z$  are the components of vector from  $i$ th to  $j$ th atom in the cartesian coordinate system fixed with respect to the molecule. The expression in bracket in (1) is seen to be the total electric field at  $i$ th atom and consists of the applied field plus the field of all other induced dipoles in the molecule—the effect of permanent dipole is omitted since it does not influence induced dipole moment. Equation (1) may be rearranged to read as

$$\alpha_i^{-1} \mu_i + \sum_{\substack{j=1 \\ j \neq i}}^N T_{ij} \mu_j = E_i. \quad (3)$$

Equation (3) represents system of  $N$ -matrix equation equivalent to the single matrix equation

$$\begin{vmatrix} \alpha_1^{-1} & T_{12} & \dots & T_{1N} \\ T_{21} & \alpha_2^{-1} & \dots & T_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ T_{N1} & \dots & \dots & \alpha_N^{-1} \end{vmatrix} \begin{vmatrix} \mu_1 \\ \mu_2 \\ \vdots \\ \mu_N \end{vmatrix} = \begin{vmatrix} E_1 \\ E_2 \\ \vdots \\ E_N \end{vmatrix}, \quad (4)$$

or briefly

$$A \mu = E. \quad (5)$$

Here  $A$  is a  $3N \times 3N$  matrix  $E$  and  $\mu$  are  $3N \times 1$  column vectors. It can be inferred

from analogy that  $T_{ij}$  is the inverse matrix of induced dipole-dipole polarizability tensor between  $i$ th and  $j$ th atoms.

$$\mu_{\text{mole}} = \sum_{i=1}^N \mu_i = \left[ \sum_{i=1}^N \sum_{j=1}^N A_{ij}^{-1} \right] E. \quad (6)$$

The sum of  $A_{ij}^{-1}$  as shown in bracket in (6) is the overall molecular polarizability. This molecular polarizability matrix is then diagonalised to give the three principal polarizability components  $a_1$ ,  $a_2$  and  $a_3$  along the vector specifying the corresponding axes of the molecule. The mean molecular polarizability is given by

$$\bar{a}_M = \frac{1}{3} (a_1 + a_2 + a_3). \quad (7)$$

The results obtained on the basis of the above theory may be used to calculate some electro-optical properties *viz.* molar refraction depolarization ratio and optical rotation.

The depolarization ratio for the light scattered in a direction perpendicular to both the direction of propagation and that of polarization of incident light is given by

$$\rho_l = 3r^2/45 (a^{-2} + 4\gamma^2), \quad (8)$$

where

$$\gamma^2 = \frac{1}{2} [(a_1 - a_2)^2 + (a_1 - a_3)^2 + (a_2 - a_3)^2]. \quad (9)$$

Here  $a_1$ ,  $a_2$  and  $a_3$  are principal polarizabilities.

A further extension of the theory leads to calculation of optical rotation. Equation (6) for induced dipole moment of  $i$ th atom of an optically active molecule leads to an expression for specific rotation when one substitutes for the field at  $j$ th atom as  $E_0 + \mathbf{r}_j \cdot \nabla E$  from a series expansion of the field of the wave about an arbitrary origin near the molecule (Appelquist 1973, 1979). Taking into account the magnetic moment contribution as well and performing averaging over all orientations, one finds for the intrinsic molar rotation  $[m]$  at wavelength  $\lambda$

$$[m] = [48 \pi^2 N/\lambda^2] \sum_{i < j} \mathbf{r}_{ij} \cdot \mathbf{b}_{ij}, \quad 10$$

where  $b_{ij}$  is a vector formed from the relay tensor in the manner

$$b_{ij} = (B_{ij}^{32} - B_{ij}^{23}, B_{ij}^{13} - B_{ij}^{31}, B_{ij}^{21} - B_{ij}^{12}); \quad 11$$

where superscripts denote cartesian components. The present molar rotation  $[M]$  is related to the conventional specific rotation  $[\alpha]$  as (Eliel 1978)

$$[M] = \frac{3}{(n^2 + 2)} \cdot [\alpha] \cdot \frac{M}{100}. \quad 12$$

### 3. Results and discussion

Both glycine and L-alanine exist in the Zwitterionic form. The molecular formulae are  $\text{N}^+\text{H}_3 - \text{CH}_2 - \text{COO}^-$  and  $\text{N}^+\text{H}_3 - \text{CH}(\text{CH}_3) - \text{COO}^-$  respectively. The optimized values of atomic polarizabilities used in the present calculation are those reported by Applequist (1979). The mean molecular polarizabilities of glycine and L-alanine as calculated by the Lippincott delta-function potential model, the atomic polarization method and the atom-dipole interaction model and those from Kerr effect measurements are given in table 1. The results of atom-dipole interaction model are in fairly good agreement with those reported from experimental measurements of Kerr effect (Orttung and Meyers 1963; Orttung and Armour 1967). The values calculated by the Lippincott delta function potential model are also close to the value of the Kerr effect measurement but those of the atomic polarization method are much lower. This is because the atomic polarization method ignores various fragment-fragment interaction while contributions due to these interactions are, to some extent, considered in the Lippincott delta-function potential model. Since the computer program was designed to take up molecules upto 10 units, the  $-\text{CH}_3$  group in L-alanine has been considered as point dipole with its polarizability centred at carbon atom. The value of  $-\text{CH}_3$  group polarizability which gave the best result for L-alanine polarizability was adjusted to be  $1.36 \text{ \AA}^3$ . The value  $6.595 \text{ \AA}^3$  for glycine polarizability was also obtained by considering  $-\text{CH}_2$  group as point dipole centred at carbon atom and with a polarizability of  $1.05 \text{ \AA}^3$ .

The values of principal polarizabilities  $a_1$ ,  $a_2$  and  $a_3$ , the refractive indices  $n_{a_1}$ ,  $n_{a_2}$ ,  $n_{a_3}$  along the direction of principal polarizability axes and the average isotropic refractive index  $n_{\bar{a}}$ , depolarization ratios  $\rho_t$  and molar rotation  $[M]$  for glycine and L-alanine are given in table 2. These results are in fairly good agreement with experimental measurements (Orttung and Armour 1967). Considerable caution is necessary in interpreting the results because of the approximations made in the theoretical analysis. The most important assumption is that the internal field is

Table 1. Mean molecular polarizabilities ( $\lambda=5893 \text{ \AA}$ )

Method	Molecule ( $\text{ \AA}^3$ )	
	Glycine	L-alanine
Lippincott delta function potential model	5.966	8.325
Atomic polarization method	5.555	6.585
Atom dipole interaction model	6.197 (6.595) <sup>a</sup>	8.367 <sup>b</sup>
Kerr effect data	6.534	8.350
Crystal <sup>c</sup>	6.300	8.200
Solution <sup>c</sup>	6.500	8.300
Bond <sup>c</sup>	7.000	8.800
Bond (adjust) <sup>c</sup>	6.400	8.200

<sup>a</sup>Glycine polarizability calculated with  $-\text{CH}_2$  as point dipole of average polarizability  $1.05 \text{ \AA}^3$

<sup>b</sup>L-alanine polarizability calculated with  $\text{CH}_3$  as point dipole of average polarizability  $1.36 \text{ \AA}^3$ .

<sup>c</sup>Orttung and Armour (1967).

**Table 2.** Principal polarizabilities, principal and average isotropic refractive indices, depolarization ratios and Molar rotation.

Property	Glycine	L-Alanine
$\alpha_1$	7·898 Å <sup>3</sup>	11·419 Å <sup>3</sup>
$\alpha_2$	6·109 Å <sup>3</sup>	7·571 Å <sup>3</sup>
$\alpha_3$	4·583	6·111 Å <sup>3</sup>
$M\alpha_1$	1·785 (1·664)	1·840 (1·583)
$M\alpha_2$	1·566 (1·616)	1·499 (1·573)
$M\alpha_3$	1·404 (1·502)	1·390 (1·520)
$n_{\alpha}^-$	1·630*	1·564 (1·606)
$\rho_{\lambda}$	1·576 (1·680)	
[M]	7·7075	9·385
		-4·647 (vacuum)
		in
		+1·600 (water)
		+13·000 (in 5 N HCl)

Figures in parenthesis refer to observed values.

\*The value of polarizability when the CH<sub>2</sub> group is regarded as a point dipole.

adequately represented by the Lorentz internal field for each principal axis direction. The molar optical rotation of L-alanine calculated from (10) and (12) and those measured in aqueous and 5 N HCl solutions are also given in table 2. As mentioned by Greenstein and Winitz (1961) the molar optical rotation values depend on the nature of the solvent and exhibit wide differences in magnitude and sign. One of the difficulties encountered in the theoretical calculations is to know the precise nature of the solute-solute and solute-solvent interactions. These have not been considered in the present calculation.

### Acknowledgement

The authors are thankful to the Department of Science and Technology, New Delhi for the grant in support of this work.

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