

Polarizability in the Structural Studies of Serine and Substituted Serines

D. Zarena^{1*}, N. Jyothi²

¹Department of Physics, JNTUA College of Engineering, Ananthapuramu, Andhra Pradesh, India, ²Department of Physics, Sri Krishnadevaraya University, Ananthapuramu, Andhra Pradesh, India

ABSTRACT

Bond and molecular polarizabilities of Serine and its derivatives have been evaluated by Lippincott δ -function model and molecular vibration methods. Structure and chemical activity of the atoms present in the molecules has been identified from these bond polarizability studies. The results are discussed in comparison with X-ray structural data and quantum chemical calculations.

Key words: Polarizability, Force constants, Mean amplitudes of vibration, Amino acid.

1. INTRODUCTION

Serine is a non-essential amino acid that is synthesized in life organisms from glycine. It has a relevant role in fat metabolism and tissue growth. It also participates in nucleic acid metabolism and in the synthesis of immunoglobulins and antibiotics. Analogues of serine have been found in cell membranes, brain proteins, and nerve coverings. This amino acid has also application in cosmetic industry as a skin moisturizer [1]. Serine phosphate is unique among the amino acid phosphates, as it occurs both in the membrane phospholipid: phosphatidyl serine. The N⁺-C-C-O chain that occurs in this compound is also present in various alkaloids, brain amines, and membrane molecules [2]. Thienyl serine can act as an antagonist for serine in protein synthesis, leading to serine deficiency [3]. In this paper, bond polarizability studies are extended to serine molecules to understand the aliphyl-aryl nature of carbon atoms.

2. MOLECULAR POLARIZABILITY

Mean molecular polarizability is generally determined from refractivity and light scattering techniques. In the present paper, bond and molecular polarizabilities of the molecules considered here are theoretically determined by (i) Lippincott δ -function potential model and (ii) molecular vibration method.

2.1. Lippincott δ -Function Potential Model

This method involves the evaluation of (i) a bond parallel component and (ii) a bond perpendicular component. The bond parallel component is obtained from the contributions of (a) bond region electrons and (b) non-bond region electrons according to the valence bond theory. The perpendicular components of polarizability are evaluated from Pauling's electronegativities and atomic polarizabilities of the atoms of the molecule. The details of this method are given in the earlier papers [4-10]. The appropriate relations are given below.

$$\alpha_{llb} = \frac{4nA}{a_0} \left[\frac{R^2}{4} + \frac{1}{2C_R^2} \right] \cdot \exp \left[-\frac{(x_A - x_B)^2}{4} \right]$$

$$\alpha_{11n} = \sum_j f_j \alpha_j$$

$$\sum 2\alpha_{\perp} = n_{df} \frac{\sum x_j^2 \alpha_j}{\sum x_j^2}$$

$$\alpha_M = \frac{1}{3} (\sum \alpha_{llp} + \sum \alpha_{11n} + \sum 2\alpha_{\perp})$$

The inter nuclear distance data required for the present work are taken from the literature [3,11-15]. Pauling's electronegativities and Lippincott's [16] atomic polarizabilities are also used in these calculations. The results are presented in Table 1.

2.2. Molecular Vibration Method

Based on the theory of the Kerr effect, Rao and Murthy [17] developed molecular vibration method. They derived equations relating longitudinal bond polarizability coefficient (b_L) with stretching force constant (K) and transverse bond polarizability coefficient (b_T) with its mean amplitude of vibration ($s^{1/2}$). The individual bond polarizability coefficients are obtained by solving the two expressions:

$$b_L - b_T = A \left[(x_1 x_2)^{\frac{1}{2}} \left(\frac{aN}{K-b} \right)^{\frac{2}{3}} \right]^{\frac{K}{(3b-2K)}}$$

$$b_L + 2b_T = Cp^{j_B} J_B^{m} \sigma^{\frac{1}{2}}$$

The meaning of the various terms is given in the earlier papers [4-10].

*Corresponding author:

D. Zarena,

E-mail: zareenajntua@gmail.com

ISSN NO: 2320-0898 (p); 2320-0928 (e)

DOI: 10.22607/IJACS.2023.1101009

Received: 05th December 2022;

Revised: 20th December 2022;

Accepted: 25th December 2022

Table 1: Molecular polarizabilities of serine and its derivatives ($\alpha_M \times 10^{23} \text{ cm}^3$).

Molecule	$\Sigma\alpha_{IIp}$	$\Sigma\alpha_{IIa}$	$\Sigma 2\alpha_{\perp}$	α_M
L-Serine	1.408	0.157	1.091	0.886
L-O-Serine phosphate	1.894	0.261	1.498	1.217
Thienyl-DL-Serine Monohydrate	2.773	0.284	1.651	1.569
L-Alanyl-L-Serine	2.615	0.197	1.823	1.545
N-Acetyl N'-methyl serine amide	2.623	0.177	1.776	1.525
N-Dodecanoyl-L-Serine Monohydrate	5.771	0.187	3.703	3.220

Using the force constants and mean amplitudes of vibration longitudinal and transverse bond coefficient values of each bond can be obtained. Finally, the molecular polarizability is given by

$$\alpha_M = \sum_i \frac{n_i (b_L + 2b_T)_i}{3}$$

where n_i is the number of bonds of type i . Using force constants data and IR and Raman frequency data [1,18-21], b_L and b_T values are estimated and presented in Table 2. A comparison of the mean molecular polarizabilities along with LeFevre method [22] is presented in Table 3.

3. RESULTS AND DISCUSSION

The longitudinal bond polarizability coefficient b_L of C'-C α bond is 0.143 (in 10^{23} cm^3 units here and elsewhere). Le Fevre bond polarizability values for C-C bond are 0.099 in aliphatic compounds like CH₃-CH₃ and 0.224 in aromatic compounds like benzene. The b_L values are in between the aliphatic and aromatic values of Le Fevre, indicating aliphyl-aryl character. The zwitter ionic structure of these molecules between C'=O and C-NH₂ groups shows a partial double bond character. Therefore, this increase in the electron density of the C-N bond will automatically increase the electron density of the C' atom and also C α atom. Hence, there will be an increase in the bond polarizability coefficient. This is exhibited by the b_L (C-C) values. Molecular vibration, which depends on bond force constant and mean amplitude of vibration, is in a position to project this property.

The bond polarizability coefficient b_L for C-N bond is 0.177 in serine. This value is much higher than the 0.057 quoted by Le Fevre in (CH₃)₃N which is a typical aliphatic amide. These b_L values compare with b_L (C-C) of aromatic linkages (0.224 in C₆H₆). The increased values of b_L show the presence of delocalized π -electrons along the C-N bonds. Since the resonance between C=O and C-N is well established, this higher b_L value appears to be meaningful. Thus, this b_L (C-N) value is in a position to show evidence for the presence of delocalized electrons from the polarizability point of view.

The values of the bond polarizability coefficient b_L for the C'=O bond are 0.171 in serine. This value is less compared to Le Fevre b_L value of 0.230 in dimethyl acetone (CH₃)₂C=O. This is an aliphatic compound basically and there is no possibility for the movement of the bond or migration of the double bond. Hence, the higher value can be understood. In the present compounds, the C=O can resonate with C-NH₂ or C-N⁺H₃ bonds, and hence, there is quite a possibility of less electron density due to delocalization of electrons. Hence, the bond polarizability in this case naturally decreases.

The b_L value of C'-O is 0.183. These bonds appear in compounds where there is no dipeptide formation, but zwitter ionic structure is noticed. The polarizability of the unpaired electron on oxygen

Table 2: Force field data and bond polarizability coefficients of serine and its derivatives ($\times 10^{23} \text{ cm}^3$).

Bond	Force constant (K) m dyne/Å	b_L	b_T	$(b_L + 2b_T)/3$
C=O	12.29	0.171	0.038	0.082
C-O	4.28	0.183	0.069	0.107
C α -C'	7.65	0.143	0.040	0.075
C α -C β	4.10	0.152	0.058	0.089
C α -H	4.92	0.076	0.064	0.068
N-H	5.33	0.093	0.084	0.087
O-H	6.91	0.104	0.096	0.099
C-N ⁺ H ₃	2.48	0.177	0.101	0.126
C-S (Ring)	1.48	0.180	0.082	0.114
P-O	5.69	0.173	0.062	0.099
P=O	10.23	0.160	0.150	0.153
C-H (methyl)	4.95	0.077	0.065	0.069

Table 3: Molecular polarizabilities of serine and its derivatives ($\alpha_M \times 10^{23} \text{ cm}^3$).

Molecule	Lippincott method	Molecular dynamics method	Le Fevre method
L-Serine	0.886	1.136	1.063
L-O-Serine phosphate	1.217	1.795	*0.821
Thienyl-DL-serine monohydrate	1.569	1.824	1.559
L-Alanyl-L-Serine	1.545	1.979	1.821
N-Acetyl N'-methyl serine amide	1.526	1.914	1.736
N-Dodecanoyl-L-serine monohydrate	3.220	3.682	1.570
			3.465

*Denotes present experimental value

(O⁻) may be responsible for this increase in bond polarizability over C=O.

The b_L value of the C-H bond is nearly 0.076 and b_T value is nearly 0.064 unlike the Le Fevre values of the 0.064 for b_L , b_T , and b_V . Le Fevre assumed that C-H bonds are isotropically polarizable. However, this is not true. Increasing evidence is available that C-H bonds are not isotropically polarizable from the literature [23].

The above results can be corroborated with the evidences drawn from X-ray crystallographic data and quantum chemical calculations.

Shortening of single bonds and elongation of double bonds is a characteristic property of resonance as evident in benzene (average C-C = 1.39 Å). Therefore, this increase in the bond length is a clear evidence of C=N character in the dipeptides studies here. Similarly, the C=O bond distances have increased up to 1.26 Å from the standard values of 1.24 Å. This is no doubt an elongation of the double bond. It is a characteristic resonance of C=O. The minimum bond length of C-O bond is found to 1.212 Å which is shorter than the normal value. Therefore, all these variations in internuclear distances are a very clear evidence of resonance between C'-O and C'-N in dipeptide units. Molecular vibrations and

molecular polarizability being functions of the changes around each bond molecule are in a position to show these effects.

From Table 3, it can be seen that there is good agreement between the mean molecular polarizabilities estimated by the three methods. The closer agreement between the Le Fevre values and the molecular vibration values indicates that a method based on molecular vibration parameters is more sensitive to structural changes.

4. CONCLUSION

Molecular dynamics method which is based on force constants and mean amplitudes of vibration from IR and Raman data are a more sensitive method. These parameters vary from molecule to molecule very sensitively and hence present a correct polarizability picture.

5. REFERENCES

1. F. J. Ramirez, I. Tunon, E. Silla, (2004) Amino acid chemistry in solution: structural properties and vibrational dynamics of serine using density functional theory and a continuum solvent model, *Chemical Physics*, **303**: 85-96.
2. E. F. Putkey, M. Sundaralingam, (1970) Molecular structures of amino acids and peptides. I. The crystal structure and conformation of DL-O-serine phosphate monohydrate. Very short phosphate-phosphate hydrogen bonds, *Acta Crystallographica*, **B26**: 782-789.
3. S. Swaminathan, K. K. Chacko, (1979) Thienyl-DL-serine Monohydrate, *Acta Crystallographica*, **B35**: 208.
4. D. Zarena, D.V. Subbaiah, (2014) Molecular polarizability in the structural studies of cytidine and its derivatives, *Indian Journal of Advances in Chemical Science*, **2(4)**: 303-306.
5. D. V. Subbaiah, V. R. K. Murthy, (2008) Conformational and microwave dielectric relaxation studies of hydrogen bonded polar binary mixtures of propionaldehyde with isopropyl amine, *Molecular Physics*, **106(1)**: 95-101.
6. D. V. Subbaiah, M. S. Sastry, V. R. Murthy, (1982) Molecular polarizability in the structural studies of halogenated pyrimidines, *Journal of Molecular Structure*, **87**: 105.
7. D. V. Subbaiah, M. S. Sastry, V. R. Murthy, (1983) Bond and molecular polarizabilities in the structural studies of thymine and its derivatives, *Journal of Physical Chemistry*, **87**: 1730-1732.
8. D. V. Subbaiah, M. S. Sastry, V. R. Murthy, (1993) Bond and molecular polarizabilities in the reactivity studies of uracil and its substituents, *Biochemical and Biophysical Research Communications*, **196**: 1422-1429.
9. D. V. Subbaiah, M. S. Sastry, V. R. Murthy, (1994) Heteroaromatic studies of purine bases, *Journal of Molecular Structure*, **41**: 319.
10. D. V. Subbaiah, M. S. Sastry, V. R. Murthy, (1997) Polarizabilities from the δ -Function Model of Chemical Binding. II. Molecules with Polar Bonds, *Asian Chemistry Letters*, **1**: 5.
11. J. Kistenmacher, A. Rand, E. Marsh, E, (1974) Refinements of the crystal structures of DL-serine and anhydrous L-serine, *Acta Crystallographica*, **B30**: 2573-2578.
12. M. Sunderlingam, E. F. Putkey, (1970) Molecular structures of amino acids and peptides, *Acta Crystallographica*, **B26**: 790-800.
13. G. Jones, L. Falvello, O. Kennard, (1978) The crystal structure of L-alanyl-L-serine, *Acta Crystallographica*, **B34**: 1939.
14. K. V. J. Klimkowski, C. V. Alsenoy, D. Ewbank, L. Schafer, (1987) Ab initio geometry refinement of some selected structures of the model dipeptide N-acetyl N'-methyl serine amide, *Journal of Molecular Structure*, **152**: 261.
15. B. Schade, J.-H. Fuhrhop, V. Hubert, M. Weber and P. Luger, (1997) Hydrogen-Bonding Networks Involving Water in Amphiphilic N-Dodecanoyl-L-serine Monohydrate, *Acta Crystallographica*, **C53**, 1070-1073.
16. E. R. Lippincott, (1964) Polarizabilities from δ -function potentials, *Journal of Physical Chemistry*, **68**: 2926.
17. B. P. Rao, V. R. Murthy, (1979) Molecular polarizabilities from molecular vibration studies, *Indian chemistry Journal*, **13**: 17-21.
18. I. D. Reva, S. G. Stepanian, A. M. Plokhotnichenko, E. D. Radchenko, G. G. Sheina, Y. P. Blagoi, (1994) Infrared matrix isolation studies of amino acids. Molecular structure of proline, *Journal of Molecular Structure*, **318**: 1-13.
19. X. Cao, G. Fisher, (2003) Crystal and molecular structure of dl-serine hydrochloride studied by x-ray diffraction, low-temperature fourier transform infrared spectroscopy and dft(b3lyp) calculations, *Journal of Molecular Structure*, **519**: 153.
20. L. I. Grace, R. Cohen, T. M. Dunn, M. Lubman, M. S. de Vries, (2002) The R2PI spectroscopy of tyrosine: A vibronic analysis, *Journal of Molecular Spectroscopy*, **215**: 204-219.
21. A. Y. Hirakawa, Y. Nishimura, T. Matsumoto, M. Nakamishi, M. Tsuboi, (1978) Characterization of a few Raman lines of tryptophan, *Journal of Raman Spectroscopy*, **7**: 282-287.
22. R. J. W. Le Fevre, (1965) *Advances in Physical Organic Chemistry*, Vol. 3, London: Academic Press, p1.
23. S. Bhagavantam, (1942) The scattering of light and raman effect, *Chemical Publishing Company*, Brooklyn, New York.

*Bibliographical Sketch



Dr. D. Zarena, did her M.Sc. in Physics and Ph.D. in Physics from Sri Krishnadevaraya University, Ananthapuramu, India. After completion of Ph.D, she worked as DBT-Postdoctoral fellow at Indian Institute of Science, Bangalore for 3 years. At present, she is working as Senior Assistant Professor and i/c Head, Department of Physics, JNTUA College of Engineering, Ananthapuramu since 2011. She has completed two research projects funded by Department of Science and Technology and University Grants Commission, Govt. of India. In 2016, she also received prestigious UGC-Raman postdoctoral fellowship to work in USA.