

Studies on Crystal Growth, Vibrational, Electronic Properties of Nonlinear Optical Crystal: Triglycine Phosphate

M.R.Meera¹, C.N. Dipuna Das¹, V. Bena Jothy¹, S.L.Rayar²

¹ Department of Physics and Research Centre,

² Department of Physics,

¹ Women's Christian College, Nagercoil, India

² St. Judes College, Thoothoor. India

¹ meeranairmrm17@gmail.com

ABSTRACT

Nonlinear optics is a topic of much current interest that exhibits a great diversity. This is due to the technological potentials of certain nonlinear optical effects for photonic based technologies. Many NLO crystals grown by mixing amino acids with various organic and inorganic acids have been reported in the literature. Hence, glycine mixed semi-organic material will be of special interest as a fundamental building block to develop many complex crystals with improved NLO properties. In this context, the present work it is attempted to grow NLO active Triglycine phosphate $[(\text{NH}_2\text{CH}_2\text{COOH})_3\text{H}_3\text{PO}_4]$ (TGP) crystal from aqueous solution at room temperature by slow evaporation method. The geometry, intermolecular hydrogen bonding and harmonic vibrational wavenumbers of TGP was investigated with the help of B3LYP density functional theory (DFT) methods. Natural Bond Orbital (NBO) analysis confirms the occurrence of strong intermolecular N-H...O hydrogen bond. Second harmonic frequency generation was examined by Kurtz and Perry powder test. Theoretical first order hyperpolarizability value was calculated.

Keywords: TGP, DFT, NBO, XRD, SHG

1. INTRODUCTION

In the modern world, the development of science in many areas has been achieved through the growth of single crystals. Large sized single crystals are essential for device fabrication and efforts are taken to grow large single crystals in short duration with less cost. Over the past two decades much attention has been paid to the search of novel high quality NLO materials that can generate high second order optical nonlinearities which is important for potential applications including telecommunication, optical computing, and optical data storage and processing [1-6]. Especially, the complexes of many inorganic derivatives and amino acids provide excellent crystals such as triglycine sulphate and L-arginine phosphate, which are accepted for the fabrication of devices [7]. One of the advantages in working with organic materials is that they allow one to fine-tune the chemical structures and properties for the desired nonlinear optical properties [8]. The molecular engineering approach has led to better understanding of the relationship between the crystal structure and its optical nonlinearities [9]. Due to their potential applications in photonic devices, bulk NLO properties of materials as well as their dependence on the first hyperpolarizabilities of molecules have evoked a lot of experimental efforts [10-12] and theoretical research [13-15]. Natural Bond Orbital (NBO) analysis can be employed to identify and substantiate the possible intra- and intermolecular interactions between the units that would form the H-bonded network [16]. Vibrational spectral studies of the molecules can be used to provide deeper knowledge about the relationships between molecular architecture, nonlinear response and hyperpolarizability. The present work describes the vibrational spectral investigations aided by DFT computations to elucidate the correlation between the molecular structure and NLO property investigating the Twisted Intra-molecular Charge Transfer (TICT) interaction, hydrogen bonds and static first hyperpolarizability of the NLO material Triglycine phosphate (TGP). Second harmonic generation (SHG) efficiency of the grown TGP crystal were studied by Kurtz powder method.

2. EXPERIMENTAL AND COMPUTATIONAL DETAILS

TGP was obtained by slow evaporation method from an aqueous solution, containing glycine and phosphoric acid in the stoichiometric ratio 3:1 and crystals were obtained within the period of 2-3 weeks. Photograph of the grown crystal is as shown in Fig 1 and the Structure of Triglycine Phosphate crystal as shown in Fig. 2. Quantum chemical density functional computations were carried out using Gaussian'09 software package [17]. Optimized molecular geometry, molecular energies and harmonic vibrational wave

numbers have been calculated using B3LYP/6-31G basis set. NBO analysis has been performed on title compound using HF level using 6-31G basis set.

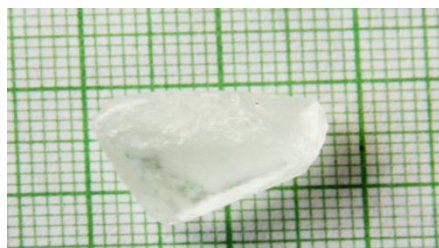


Fig 1 Grown pure TGP crystal

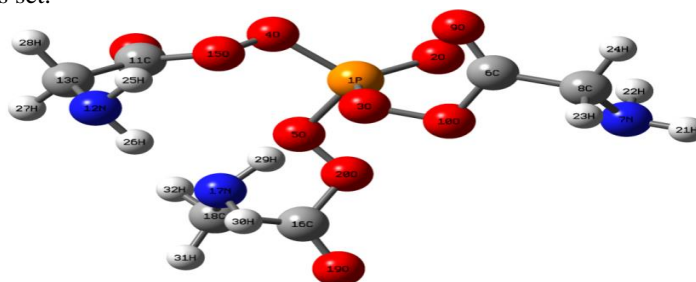


Fig. 2 Structure of Triglycine Phosphate crystal

3. RESULT AND DISCUSSIONS

3.1. SINGLE CRYSTAL XRD

Single crystal XRD has been carried out using Enraf nonius-cad4 diffractometer. The data obtained show that the grown crystal of Triglycine phosphate crystal belongs to monoclinic system with lattice Parameters $a = 5.094 \text{ \AA}$, $b = 11.984 \text{ \AA}$, $c = 5.453 \text{ \AA}$, $\alpha = \gamma = 90^\circ$ and $\beta = 111.70^\circ$.

3.2. OPTIMIZED STRUCTURE

Optimized geometrical parameters such as bond lengths, bond angles and dihedral angles calculated using B3LYP /6-31G basis set have been listed in Table.1 and the optimized structure is shown in Fig.2. Twisting of amino group with respect to other groups of the molecules and distortion of carbon-carbon skeleton obviously illustrate the influence of NH_2^+ group on the structural conformation of the TGP crystal due to the formation of strong hydrogen bonding network. However, the twist of the glycine, which is prerequisite to make the crystal NLO active, can be introduced by the Twisted Intramolecular Charge Transfer (ICT) due to the presence of strong ionic intra-molecular N-H...O hydrogen bonding. $\text{C}_6\text{-O}_9$ and $\text{C}_{11}\text{-O}_{14}$ bond lengths are measured to be 1.193 and 1.192 \AA in TGP. The dihedral angles $\text{O}_9\text{-C}_6\text{-C}_8\text{-N}_7$ and $\text{O}_{14}\text{-C}_{11}\text{-C}_{13}\text{-N}_{12}$ of the glycine skeleton in TGP are calculated to be 130.14° and 151.27° for the DFT calculations with 6-31G(d) basis set. It is also inferred that the glycine skeleton in TGP is reasonably twisted.

Table: 1 Optimized Bond lengths (\AA), Bond angles ($^\circ$) and Dihedral angle ($^\circ$) of TGP by B3LYP/6-31G basis sets

Bond Length	Theo. (\AA)	Bond angle	Theo. ($^\circ$)	Dihedral angle ($^\circ$)	Theo. ($^\circ$)
$\text{P}_1\text{-O}_4$	1.6988	$\text{O}_2\text{-P}_1\text{-O}_5$	111.5301	$\text{O}_3\text{-P}_1\text{-O}_4\text{-O}_{15}$	49.6827
$\text{P}_1\text{-O}_5$	1.705	$\text{O}_3\text{-P}_1\text{-O}_4$	112.4421	$\text{O}_5\text{-P}_1\text{-O}_4\text{-O}_{15}$	52.3624
$\text{O}_3\text{-O}_{10}$	1.4341	$\text{O}_3\text{-P}_1\text{-O}_5$	108.6353	$\text{O}_2\text{-P}_1\text{-O}_5\text{-O}_{20}$	61.5947
$\text{C}_6\text{-C}_8$	1.516	$\text{O}_4\text{-P}_1\text{-O}_5$	128.7513	$\text{O}_3\text{-P}_1\text{-O}_5\text{-O}_{20}$	67.3435
$\text{C}_6\text{-O}_9$	1.1933	$\text{P}_1\text{-O}_3\text{-O}_{10}$	109.105	$\text{O}_4\text{-P}_1\text{-O}_5\text{-O}_{20}$	171.8424
$\text{C}_6\text{-O}_{10}$	1.4048	$\text{P}_1\text{-O}_4\text{-O}_{15}$	122.1436	$\text{P}_1\text{-O}_3\text{-O}_{10}\text{-C}_6$	94.5827
$\text{N}_7\text{-C}_8$	1.4339	$\text{P}_1\text{-O}_5\text{-O}_{20}$	117.8303	$\text{P}_1\text{-O}_4\text{-O}_{15}\text{-C}_{11}$	122.5802
$\text{C}_8\text{-H}_{23}$	1.0826	$\text{C}_8\text{-C}_6\text{-O}_9$	117.579	$\text{P}_1\text{-O}_5\text{-O}_{20}\text{-C}_{16}$	155.1943
$\text{C}_8\text{-H}_{24}$	1.0795	$\text{C}_8\text{-C}_6\text{-O}_{10}$	114.7042	$\text{O}_9\text{-C}_6\text{-C}_8\text{-N}_7$	130.1452
$\text{C}_{11}\text{-O}_{14}$	1.1925	$\text{C}_8\text{-N}_7\text{-H}_{22}$	105.7776	$\text{O}_9\text{-C}_6\text{-C}_8\text{-H}_{23}$	107.0978
$\text{C}_{11}\text{-O}_{15}$	1.406	$\text{H}_{21}\text{-N}_7\text{-H}_{22}$	109.7259	$\text{O}_9\text{-C}_6\text{-O}_{10}\text{-O}_3$	1.3119
$\text{N}_{12}\text{-C}_{13}$	1.4279	$\text{C}_6\text{-C}_8\text{-N}_7$	110.5203	$\text{H}_{21}\text{-N}_7\text{-C}_8\text{-C}_6$	74.2357
$\text{N}_{12}\text{-H}_{25}$	0.9917	$\text{C}_6\text{-C}_8\text{-H}_{23}$	107.6533	$\text{H}_{21}\text{-N}_7\text{-C}_8\text{-H}_{23}$	47.4137
$\text{N}_{12}\text{-H}_{26}$	0.9937	$\text{C}_6\text{-C}_8\text{-H}_{24}$	112.7495	$\text{H}_{21}\text{-N}_7\text{-C}_8\text{-H}_{24}$	165.9811
$\text{C}_{13}\text{-H}_{27}$	1.0807	$\text{N}_7\text{-C}_8\text{-H}_{23}$	127.2068	$\text{H}_{22}\text{-N}_7\text{-C}_8\text{-C}_6$	69.7551
$\text{C}_{16}\text{-C}_{18}$	1.5112	$\text{H}_{23}\text{-C}_8\text{-H}_{24}$	122.5735	$\text{H}_{22}\text{-N}_7\text{-C}_8\text{-H}_{23}$	168.5955
$\text{C}_{16}\text{-C}_{19}$	1.1936	$\text{O}_3\text{-O}_{10}\text{-C}_6$	118.3265	$\text{H}_{22}\text{-N}_7\text{-C}_8\text{-H}_{24}$	50.0281
$\text{C}_{16}\text{-O}_{20}$	1.4157	$\text{C}_{13}\text{-C}_{11}\text{-O}_{14}$	118.4266	$\text{O}_{14}\text{-C}_{11}\text{-C}_{13}\text{-N}_{12}$	151.2711
$\text{N}_{17}\text{-C}_{18}$	1.4462	$\text{C}_{13}\text{-C}_{11}\text{-O}_{15}$	115.8295	$\text{O}_{14}\text{-C}_{11}\text{-C}_{13}\text{-H}_{27}$	27.4381

3.2. NATURAL BOND ORBITAL ANALYSIS

NBO analysis provides an electronic structure description akin to the classic Lewis bonding theory. Delocalization of electron density between occupied Lewis type (bond or lone pair) NBO orbital and formally unoccupied (antibonding) non-Lewis NBO orbital correspond to a stabilizing donor-acceptor interaction can be described as a hyperconjugative electron transfer process from the donor (filled) to the acceptor (vacant) orbital [18-21]. NBO analysis has been performed on title compound using HF level using 6-31G basis set. Change in electron density in the (σ^* , π^*) antibonding orbital and electronic energy have been calculated to give clear evidence of stabilization originating from various molecular interactions. Stabilization energy associated with hyperconjugative interactions $LP_1(O_5)-\sigma^*(C_{18}-H_{31})$, is obtained as 0.73 kJ/mol (Table.2) which reveals C-H...O hydrogen bonding. Interaction involving Nitrogen having stabilization energies 3.10, 2.80, 2.56, 2.06, 2.03, 1.19 kJ/mol results in C-H...N interactions. Intra-molecular interaction is formed by the orbital overlap between $\sigma(P_1-O_3)$ and $\sigma^*(P_1-O_3)$, $\sigma(P_1-O_4)$ and $\sigma^*(P_1-O_4)$ results in intra-molecular charge transfer causing stabilization of the system. Analysis of bond length and angle for the title compound shows that there exists N-H...O hydrogen bonding between H_{29} and N_{17} due to the interaction between the lone pair of $LP_2(O_5)-\sigma^*(N_{17}-H_{29})$ with stabilization energy of 0.57 kJ/mol. Besides the intra-molecular H-bonds, Table 2 also includes the energies of the remote interactions between phosphorous-oxygen lone pairs.

Table 2: Second order perturbation theory analysis of Fock matrix in NBO basis.

Donor (i)	ED(i) (e)	Acceptor (j)	ED(j) (e)	E(2) ^a (kJ mol ⁻¹)	E(j)-E(i) ^b (a.u)	F(i,j) ^c (a.u)
LP_1O_5	1.98595	$\sigma^*C_{18}-H_{31}$	1.95298	0.73	1.77	0.032
LP_2O_5	1.96468	$\sigma^*N_{17}-H_{29}$	0.00859	0.57	1.41	0.025
LP_1N_{12}	1.95193	$\sigma^*C_{13}-H_{27}$	0.01275	3.10	1.12	0.053
LP_1N_{17}	1.95298	$\sigma^*C_{18}-H_{32}$	0.01341	2.80	1.15	0.051
LP_1N_7	1.95364	$\sigma^*C_8-H_{24}$	0.01191	2.56	1.13	1.049
LP_1N_7	1.95364	$\sigma^*C_8-H_{23}$	0.01239	2.06	1.11	0.043
LP_1N_{12}	1.95193	$\sigma^*C_{13}-H_{28}$	0.01183	2.03	1.11	0.043
LP_1N_{17}	1.95298	$\sigma^*C_{18}-H_{31}$	1.95298	1.19	1.15	0.033
σP_1-O_2	1.96655	$\sigma^*P_1-O_5$	0.17761	5.62	1.23	0.077
σP_1-O_3	1.96680	$\sigma^*P_1-O_3$	0.18027	0.83	1.19	0.029
σP_1-O_4	1.96440	$\sigma^*P_1-O_4$	0.15400	0.61	1.22	0.025
σP_1-O_5	1.96712	$\sigma^*P_1-O_4$	0.15400	7.78	1.22	0.090
σP_1-O_2	1.96655	$\sigma^*P_1-O_3$	0.18027	7.74	1.22	0.090
$\sigma C_{18}-H_{32}$	1.97605	$\pi^*C_{16}-O_{19}$	0.09291	7.53	0.94	0.076
σC_8-H_{23}	1.97159	$\sigma^*C_6-O_9$	0.01424	7.60	0.87	0.074
σC_8-H_{24}	1.97513	$\sigma^*C_6-O_{10}$	0.11425	7.07	1.16	0.083
$\pi C_{16}-O_{19}$	1.99124	$\sigma^*N_{17}-C_{18}$	0.00625	2.11	1.24	0.046
$\pi C_{16}-O_{19}$	1.99124	$\sigma^*C_{18}-H_{32}$	0.01341	1.78	1.36	0.044
$\sigma C_{13}-H_{27}$	1.97326	$\sigma^*C_{18}-H_{32}$	0.01341	4.39	1.53	0.073

a-E(2) means energy of hyperconjugative interactions; b-Energy difference between donor and acceptor i and j NBO orbitals; c-F(i,j) is the Fock matrix element between i and j NBO orbitals.

3.3. SECOND HARMONIC GENERATION (SHG) STUDIES

Kurtz and Perry method [22] was employed to measure the SHG efficiency of the grown crystals in reference with the pure KDP. In the measurement Q-switched High Energy Nd:YAG Laser (QUANTA RAY Model) Model HG-4B-High efficiency, angle tuned and temperature stabilized Second harmonic and Third harmonic Generator Crystals. Energy: 850 mJ, 450 mJ & 220 mJ: Repetition rate: 10 Hz was used. The output was measured at wavelength 532nm. SHG signal of 11.82 mJ for TGP crystal was obtained for an input energy of 0.68 J. But the standard KDP crystal gave an SHG signal of 17.3 mJ for the same input energy. Thus, it is observed that the SHG efficiency of the grown single crystal is 0.68 times that of the standard KDP crystal.

3.4. NON-LINEAR OPTICAL EFFECTS

The linear polarizability and first hyperpolarizability have been computed using B3LYP/6-31G basis set. Calculated first order hyperpolarizability components, the electronic dipole moment (μ), polarizability (α) and the first hyperpolarizability (β) are listed in Table 3. The calculated dipole moment μ_{tot} , polarizability α_{tot} , anisotropy of the polarizability $\Delta\alpha$ and first hyperpolarizability β_{tot} for title compound are given in Table 3. The calculated total dipole moment of TGP is approximately two times greater than that of urea and first

hyperpolarizability is approximately equal to that of urea indicating that the title compound is a good candidate of NLO materials.

Table 3: Calculated dipole moments (D), polarizability and first hyperpolarizability components (a.u.) for the title compound.

μ_x	1.0124593	β_{xxx}	-66.7207405
μ_y	0.2254596	β_{xxy}	-0.9157282
μ_z	-1.9174315	β_{xyy}	63.093937
μ	2.18001	β_{yyy}	-5.4247602
α_{xx}	119.3427365	β_{xxz}	-49.3908528
α_{xy}	5.743344	β_{xyz}	-16.0134918
α_{yy}	129.8889271	β_{yyz}	-19.0933638
α_{xz}	19.0741321	β_{xzz}	-23.4363083
α_{yz}	2.7867068	β_{yzz}	2.8703203
α_{zz}	126.3810348	β_{zzz}	-16.2253059
α_0	125.2042	β_{tot}	88.9953
$\Delta\alpha$	206.9169		

CONCLUSIONS

A single crystal of TGP was grown by slow evaporation technique. The twisted intra-molecular charge transfer resulting from the strong ionic hydrogen bonding among the different charged species, and its relevance in making the crystal TGP to be NLO active. Optimized geometry of the molecule shows twisted Intra-molecular Charge Transfer (ICT) due to the presence of strong ionic intra-molecular N-H...O hydrogen bonding. NBO analysis substantiates the weak C-H...O and N-H...O hydrogen bond, which is consistent with the analysis of molecular structure. SHG studies reveal that TGP crystal is a good candidate for NLO applications. Calculated first order hyperpolarizability indicates that TGP crystal is a potential candidate for NLO applications.

ACKNOWLEDGEMENT

The author Meera.M.R. thanks the University Grants Commission (UGC), India, for the award of a Teacher Fellowship under FDP scheme leading to the Ph.D. degree.

REFERENCES

- [1] M.D. Aggarwal, J.J. Stephens .*Optoelectron. Adv. Mater.* 5 (2003) 3.
- [2] C. Razzetti, M. Ardoino, C. Paorici . *Cryst. Res. Technol.* 37 (2002) 456.
- [3] J. McArdle, J.N. Sherwood, A.C. Damask . *J. Cryst. Growth* 22 (1974) 193.
- [4] E.M. Hampton, B.S. Shah, N. Sherwood . *J. Cryst. Growth* 22 (1974) 22.
- [5] S. Dhaushkodi, K. Vasantha . *Cryst. Res. Technol.* 39 (2004) 3.
- [6] H.L. Shat . *Bull. Mater. Sci.* 17 (1994) 1233.
- [7] Dacko S., Czaplak Z., Baran J., Drozd M., *Phys.Lett. A*, 223 (1996), 217.
- [8] A. Datta, S.K. Pati, *J. Chem. Phys.* 118 (2003) 8420–8427.
- [9] M.N. Bhat, S.M. Dharma prakash, *J. Cryst. Growth* 236 (2002) 376–380.
- [10] S. Debrusa, M. Maya, J. Baryckib, T. Glowiac, A.J. Barnesd, H.Ratajczak, D. Xuef, *J. Mol. Struct.* 661-662 (2003) 595.
- [11] A.A. Sukhorukov, S. Kivshar Yu, *J. Opt. Soc. Am. B* 19 (2002)772.
- [12] G. Maroulis, *J. Chem. Phys.* 113 (2000) 1813.
- [13] S.F. Mingaleev, S. Kivshar Yu, *Opt. Photon. News* 13 (2002) 48.
- [14] B.A.S. Mendis, K.M.N. de Silva, *J. Mol. Struct. (Theochem)* 678(2004) 31.
- [15] S.P. Liyanage, R.M. de Silva, K.M.N. de Silva, *J. Mol. Struct.(Theochem)* 639 (2003)195.
- [16] M. Montejo, A. Navarro, G.J. Kealey, J. Vazquez, J.J.L. Gonzalez, *J. Am. Chem. Soc.* 126 (2004) 15087.
- [17] Frisch, M. J et al. *Gaussian 09*, Revision D.01, Gaussian, Inc., Wallingford CT, 2009.
- [18] Weinhold, F.; Landis, C. R. *Valency and bonding: A Natural Bond Orbital Donor-Acceptor Perspective*; Cambridge University Press: NewYork, 2005.
- [19] Weinhold, F.; Landis, C. R. *Chem. Educ. Res. Pract.* 2001, 2, 91.
- [20] Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* 1988, 88, 899.
- [21] Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* 1980, 102, 7211.
- [22] S.K. Kurtz, T.T. Perry, *A Powder Technique for the Evaluation of Nonlinear Optical Materials*, *J. Appl. Phys.* 39 (1968) 3798.