After achieving the targeted molecules, we made an effort to explore the physical and pharmacological properties. NLO being a primary condition to a compound to act as a biosensor, chemosensor and LED.

In recent years, the research towards the development of novel organic NLO materials have found new outlook due to their structural flexibility and fast response time which make them promising prospect for optical limiting and optical switching¹⁻⁶.

Density functional theory (DFT) is a computational modeling method used in physics, chemistry and materials science. This theory has been developed recently than other *ab initio* methods.

Because of their potential applications in the optoelectronic devices, materials with nonlinear optical (NLO) properties are currently attracting considerable importance. These materials are used in telecommunications, information storage; optical switching, signal processing and terahertz wave generation (THz)⁷⁻⁹. DFT theory has been exclusively used in the prediction of many physical and chemical properties of the compound. The surface morphology, energy gap and other properties of any compounds can be predicted and the ability of the compound to act as corrosion inhibitors have also been studied ¹⁰.

Recently DFT studies were used to find the nonlinear optical property of the compounds by means of their hyperpolarisability.

First hyperpolarisability, is a measure of the nonlinear optical activity of any molecular system and is associated with intramolecular charge transfer resulting from electron transfer in a conjugated system from electron donor to electron acceptor groups within a molecule. The design of new molecules with a high charge transfer is an important part of this, because intra molecular charge transfer will lead to a very high value for hyperpolarisability.

The theoretical prediction of non linear optical properties for this kind of materials is a very important step towards the design of nonlinear optical materials. Determination of polarizabilities and hyperpolarizabilities in the gas phase is necessary for it. Density functional theory (DFT) calculations are excellent tool to predict the dipole moments, polarizability, and hyperpolarizabilities of the new materials. In this context, we intend to study the nonlinear optical property of our compound by theoretical and experimental means.

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Considering the influence of quinoline heterocycles in NLO materials, in this chapter, we study the nonlinear optical properties of triazino quinolines, pyridazino quinolines, azetidino quinolines, imidazolidino quinolines and thiazolidino quinolines using *ab initio* and density functional theory (DFT) calculations. Based on the DFT calculations few of the synthesised compounds were selected for Z-scan characterisation which is an important and prior tool for a compound to choose as a nonlinear optical material.

4.1 DFT studies for calculating NLO property.

All calculations were done by using Gaussian 09W package of programs. Gaussian 09W has already proved to be an important tool predicting molecular structures, molecular origins of NLO properties. The geometries of the compounds were optimized by Becke's three parameter hybrid functional for exchange combined with the correlation functional using 6-31G (d,p) basis set. DFT/B3LYP/6-31G (d,p) has been found to be an accurate formalism for calculating the geometrical, electronic structures and optical properties of many organic molecules.

Non linear optical effects

The interactions of electromagnetic radiation in some molecules can give a non-linear optical (NLO) effect which shows some alterations in- phase, frequency and amplitude from the incident field. Thus the NLO property of the material is theoretically calculated using mean polarizability (α_0), the total static dipole moment (μ) and the first order hyperpolarizability (β_0) with respect to x, y, z components using the equation given below and tabulated in **Table 4-11**.

Route section used for polarizability calculation is

B3LYP/6-31G (d,p) polar

$$\mu = (\mu x^{2} + \mu y^{2} + \mu z^{2})^{1/2}$$

$$\alpha_{0} = 1/3 (\alpha_{XX} + \alpha_{YY} + \alpha_{ZZ}) - ... (1)$$

$$\beta_{0} = (\beta x^{2} + \beta y^{2} + \beta z^{2})^{1/2} - ... (2)$$

$$\beta x^{2} = (\beta_{XXX} + \beta_{XYY} + \beta_{XZZ})^{2}$$

$$\beta y^{2} = (\beta_{YYY} + \beta_{YXX} + \beta_{YZZ})^{2}$$

$$\beta z^{2} = (\beta_{ZZZ} + \beta_{ZXX} + \beta_{ZYY})^{2}$$

The dipole moment, polarizability and hyperpolarisability of the synthesized compounds were calculated using the equations (1) and (2) and were tabulated. The results obtained from the calculations were tabulated and the values were compared

with that of urea $(0.11 \times 10-30 \text{esu})^{11}$, since it is one of the molecules used in the study of the NLO properties of the molecules. And the values obtained for urea was used as the threshold value for the compounds.

Gaussian outputs are reported in atomic units, so the calculated values were converted to esu [α (1au= 0.1482x10⁻²⁴ esu) β (1au=8.639x10⁻³⁰esu)].

4.11 Calculated dipolemoment (μ) polarizability (α) and hyperpolarisability (β) of substituted 4'-methyl-3-thioxo 1,2,4-triazino-quinolin-5-one (14a-g).

Comp.	μ_{total}	α_{total} esu	β_x^2	β_y^2	β_z^2	β _{total} esu
14a	6.57	33.11×10^{-24}	30130.02	1410.75	0.38	1.53×10^{-30}
14b	7.13	32.46x10 ⁻²⁴	41347.16	1656.49	0.07	1.79x10 ⁻³⁰
14c	6.95	30.71×10^{-24}	33323.99	1079.18	1.05	1.60×10^{-30}
14d	7.38	32.55 x10 ⁻²⁴	47502.20	1320.60	0.09	1.91×10^{-30}
14e	7.92	33.02×10^{-24}	40276.48	1641.06	0.007	1.77×10^{-30}
14f	7.04	36.84x10 ⁻²⁴	2149.45	9721.96	.2025	0.94×10^{-30}
14g	6.25	37.55 x10 ⁻²⁴	37094.76	2331.92	0.2209	1.72×10^{-30}

Table-4 μ , α and β of substituted 4'-methyl-3-thioxo 1,2,4-triazino-quinolin-5-one 14(a-g).

From the **Table-4** it was found that unsubstituted 4-methyl triazino quinoline, **4'-methyl-3-thioxo1,2,4-triazino-quinolin-5-one (14d)** possess hyperpolarisibility approximately **15** times greater than that of urea. In general when H atom is replaced by $-CH_3$ group at the R₁, R₂ and R₃ positions hyperpolarisibility values increased further. Also when H atom at R₁ and R₃ is replaced by -Cl the hyperpolarizability values are higher when compared with unsubstituted derivatives.

4.12 Calculated dipolemoment (μ) polarizability (α) and hyperpolarisability	t y (β)
of substituted 4'-phenyl-3-thioxo 1,2,4-triazino-quinolin-5-one (18a-g).	

Comp	μ_{total}	a _{total} esu	β_x^2	β_y^2	β_z^2	β _{total} esu
18a	6.86	42.19×10^{-24}	71786.48	7.84	6.97	2.31×10^{-30}
18b	7.40	42.50 x10 ⁻²⁴	36576.56	1.28	0.02	1.65×10^{-30}
18c	7.630	42.48×10^{-24}	93049.40	434.31	0.03	2.64×10^{-30}
18d	7.26	40.39x10 ⁻²⁴	76961.86	901.80	8.47	2.41×10^{-30}
18e	5.8396	47.32×10^{-24}	55875.50	8734.77	3.50	2.20×10^{-30}
18f	7.53	43.59x10 ⁻²⁴	67751.04	10213.12	0.09	2.41×10^{-30}
18g	8.3705	42.13x10 ⁻²⁴	78854.26	413.31	0.74	2.43×10^{-30}

Table-5 μ , α and β of substituted 4'-phenyl-3-thioxo 1,2,4-triazino-quinolin-5-one 18a-g

When methyl group at position **4'** is replaced by phenyl group a prominent increase in hyper polarisibility values were found.

But in this case all the derivatives showed approximately equal values in hyper polarisibility and it was found that the average value is **21** times greater than that of urea.

4.13 Calculated dipolemoment (μ) polarizability (α) and hyperpolarisability	ty (β)
of substituted 4'-phenyl-3-thioxo-1,2,4-triazinoquinolin-5-one (22a-g).	

Comp.	μ_{total}	α_{total} esu	β_x^2	β_y^2	β_z^2	β _{total} esu
22a	7.91	38.28×10^{-24}	53319.43	1017.61	174.50	2.08×10^{-30}
22b	5.34	39.98x10 ⁻²⁴	32263.34	129.96	92.54	1.6×10^{-30}
22c	8.04	33.76×10^{-24}	86683.14	103.02	550.84	2.55×10^{-30}
22d	4.87	41.36x10 ⁻²⁴	6006.25	14460.06	214.68	1.2×10^{-30}
22e	6.90	37.00×10^{-24}	57700.84	2729.02	1137.04	2.14×10^{-30}
22f	2.0859	49.46x10 ⁻²⁴	5550.25	705.43	4719.69	0.91×10^{-30}
22g	5.81	42.94×10^{-24}	45275.33	2157.60	939.42	1.9×10^{-30}

Table-6 μ, α and β of substituted 4'-phenyl-3-thioxo-1,2,4-triazinoquinolin-5-one 22a-g

When the position of phenyl group changed from 4' to 2', the hyper polarisibility values decreased while compared with the values of 4-phenyl substituted derivatives but with respect to 4-methyl derivatives the values were higher. Among the 2-phenyl derivatives the derivative with $-CH_3$ group at 6th position showed highest hyper polarisibility and derivative with -Cl atom at C-7 position exhibited lowest value.

As seen from table **4**, **5** and **6** hyperpolarisibility values of 4-methyl, 4-phenyl and 2-phenyl substituted triazino quinolines have not much difference. But for phenyl substituted derivatives the values increased. It may be due to the incorporation of a highly conjugated phenyl ring.

4.14 Calculated dipolemoment (μ) polarizability (α) and hyperpolarisability (β) of substituted 5-phenyl-1,4-trihydro-2*H*-pyridazino [3,4-*b*] quinolin-3-one (24a-g) (linear)

Comp	μ_{total}	a _{total} esu	β_x^2	β_y^2	β_z^2	β _{total} esu
24a	2.27	29.20×10^{-24}	296.83	3094.55	4.44	0.50×10^{-30}
24b	6.49	28.04×10^{-24}	81380.51	250.35	72.23	2.47×10^{-30}
24c	5.82	30.28×10^{-24}	27208.50	1474.56	93.12	1.47×10^{-30}
24d	5.14	25.90×10^{-24}	42352.45	2281.64	139.97	1.83×10^{-30}
24e	3.21	36.17×10^{-24}	18764.53	65.02	18.38	1.18×10^{-30}
24f	2.11	33.34×10^{-24}	10890.24	361.73	26.21	0.92×10^{-30}
24g	3.44	35.89x10 ⁻²⁴	13364.45	3247.72	519.40	1.13×10^{-30}

Table-7 μ, α and β of Substituted 5-phenyl-1,4-trihydro-2*H*-pyridazino [3,4-*b*]

quinolin-3-one 24a-g (linear)

As far as the pyridazinones are concerned linearly fused **7-methyl-5-phenyl-1,4-trihydro-2***H***-pyridazino [3,4-***b***] quinolin-3-one (24b) exhibited higher value for hyperpolarisibility and hence possess a good nonlinear optical property as compared to other derivatives.**

4.15 Calculated dipolemoment (μ) polarizability (α) and hyperpolarisability (β) of substituted 5-phenyl-1,4-trihydro-2*H*-pyridazino[3,4-*b*] quinolin-3-one26a-g (angular)

Com	μ_{total}	α_{total} esu	$\beta_{\rm x}^{2}$	β_y^2	β_z^2	β _{total} esu
26a	7.68	23.25 x10 ⁻²⁴	87255.25	15210.29	.005	2.76×10^{-30}
26b	2.9892	30.70×10^{-24}	2957.18	4261.48	17.47	0.73×10^{-30}
26c	7.61	21.69×10^{-24}	97144.32	660.49	44.62	2.70×10^{-30}
26d	2.49	26.46 x10 ⁻²⁴	3594.24	173.31	1.94	$0.53 \text{ x} 10^{-30}$
26e	2.17	31.82×10^{-24}	7834.02	2299.20	10.50	0.87×10^{-30}
26f	3.85	30.63 x10 ⁻²⁴	19509.44	1430.35	33.19	1.25 x10 ⁻³⁰
26g	3.65	29.48 x10 ⁻²⁴	15373.52	1321.32	14.21	1.12×10^{-30}

Table-8 μ, α and β of Substituted 5-phenyl-1,4-tri hydro-2*H*-pyridazino [3,4-*b*] quinolin-3-one26a-g (angular)

Among angularly fused substituted pyridazinones, 7-methyl-5-phenyl-1, 4-tri

hydro-2H-pyridazino [3,4-b] quinolin-3-one (26a) displayed highest value.

Comparing the hyperpolarizability values of linear and angular pyridazinones

7-methyl-5-phenyl-1,4-trihydro-2*H***-pyridazino [3,4-***b***] quinolin-3-one (26a)** was found to be the most effective NLO material.

4.16 Calculated dipolemoment (μ) polarizability (α) and hyperpolarisability (β) of substituted 3-chloro-1-((quinolin-2-yl)amino)-4-(2-hydroxyphenyl) azetidin-2-one 28(a-d),32(a-d),36(a-d).

Com	µ _{total}	a _{Total} esu	β_x^2	β_y^2	β_z^2	β _{total} esu
28a	3.56	32.19×10^{-24}	4104.96	3927.53	10.37	0.77×10^{-30}
28b	2.66	37.32×10^{-24}	87.05	2634.77	936.36	0.51×10^{-30}
28c	3.76	33.74x10 ⁻²⁴	2062.07	5884.42	241.80	079x10 ⁻³⁰
28d	4.25	31.72×10^{-24}	5827.80	3958.93	31.36	0.86×10^{-30}
32a	8.97	35.14×10^{-24}	78669.0	18520.4	21975.1	2.98×10^{-30}
32b	5.60	40.18×10^{-24}	21135.3	88.55	20294.8	1.76×10^{-30}
32c	7.19	34.73×10^{-24}	60653.8	1958.95	12730.6	2.37×10^{-30}
32d	3.95	38.55x10 ⁻²⁴	4810.81	1097.60	10483.7	1.11×10^{-30}
36 a	7.01	47.47×10^{-24}	4968.84	40517.6	1645.92	1.87×10^{-30}
36b	5.03	46.56x10 ⁻²⁴	9036.40	3316.61	164.87	0.97×10^{-30}
36c	5.51	$45.17 \text{x} 10^{-24}$	1526.46	12602.3	5876.76	1.22×10^{-30}
36d	5.44	44.10×10^{-24}	40860.5	740.93	1860.20	1.80×10^{-30}

Table-9 μ , α and β of substituted 3-chloro-1-((quinolin-2-yl)amino)-4-(2-hydroxyphenyl)

azetidin-2-one 28(a-d),32(a-d),36(a-d)

4.17 Calculated dipolemoment (μ) polarizability (α) and hyperpolarisability (β) of substituted 3-((quinolin-2-yl) amino)-2-(2-hydroxyphenyl) imidazolidin-4-one 29(a-c), 33(a-c), 37(a-c).

Com.	μ_{total}	α_{total} esu	β_x^2	β_y^2	β_z^2	β_{total} esu
29a	2.71	34.02×10^{-24}	7707.08	160.28	8290.10	1.10×10^{-30}
29b	1.01	30.24×10^{-24}	1495.37	464.83	0.23	0.38×10^{-30}
29c	0.97	34.21x10 ⁻²⁴	2670.82	45.16	929.03	0.521x10 ⁻
33a	0.32	38.41x10 ⁻²⁴	9886.60	1.93	422.92	0.88×10^{-30}
33b	1.47	38.20x10 ⁻²⁴	5444.79	42.34	411.04	0.66×10^{-30}
33c	1.56	39.02x10 ⁻²⁴	412.18	2722.35	150.93	0.50×10^{-30}
37a	0.32	38.95x10 ⁻²⁴	9888.31	1.90	423.12	0.88×10^{-30}
37b	1.47	38.19x10 ⁻²⁴	5443.49	42.25	410.87	0.66×10^{-30}
37c	1.56	39.21x10 ⁻²⁴	409.25	2722.75	151.04	0.50×10^{-30}

Table-10 μ, α and β of substituted 3-((quinolin-2-yl) amino)-2-(2-hydroxyphenyl)

imidazolidin-4-one 29(a-c), 33(a-c), 37(a-c)

4.18 Calculated dipolemoment (μ) polarizability (α) and hyperpolarisability (β) of substituted 3-((quinolin-2-yl)amino)-2-(2-hydroxyphenyl) thiazolidin-4-one 30(a-c),34(a-c),38(a-c).

Com	μ_{total}	α_{total} esu	β_x^2	β_y^2	β_z^2	β _{total} esu
30 a	2.14	35.80x10 ⁻²⁴	2403.73	62.00	60.88	0.434×10^{-30}
30b	2.38	33.21x10 ⁻²⁴	2710.70	617.86	6585.96	0.860×10^{-30}
30c	1.51	34.66x10 ⁻²⁴	5397.74	5292.32	211.97	0.903×10^{-30}
34 a	2.97	40.51x10 ⁻²⁴	4103.68	1941.28	8.18	0.67×10^{-30}
34b	4.20	39.05×10^{-24}	19151.79	5139.46	8332.04	1.56×10^{-30}
34c	3.71	39.70x10 ⁻²⁴	1716.44	51651.65	1202.70	2.02×10^{-30}
38 a	2.68	$46.47 \text{x} 10^{-24}$	702.78	1510.44	7136.87	0.84×10^{-30}
38b	4.20	39.05×10^{-24}	19151.79	5139.46	8332.04	1.56×10^{-30}
38c	1.93	41.89x10 ⁻²⁴	489.29	357.97	4330.96	0.621×10^{-30}

Table-11 μ, α and β of substituted 3-((quinolin-2-yl)amino)-2-(2-hydroxyphenyl)thiazolidin-4-one 30(a-c),34(a-c),38(a-c)

When comparing the hyperpolarisability of the compounds derived from schiff base viz azetidinones, imidazolidinones and thiazolidinones, azetidinones showed higher value.

4.2 Z Scan technique

Z-scan technique was introduced by Mansoor Sheik-Bahae *et al* in 1989¹². It is a popular experimental technique to measure nonlinear susceptibilities of materials.

In Z-scan, a sample is moved in the z direction along the optical axis of a tightly focused Gaussian laser beam, around its focus and the far field intensity is measured as function of sample position. Hence the method has been referred as Z-scan. The basic phenomenon behind this is the optical Kerr effect¹³.

The Z-scan measurements in the ns regime were done using the standard open aperture Z-scan technique developed by M. Sheik Bahae $et.al^{12}$.



Fig (10) Experimental Setup for Z Scan technique

The Z-scan measurements were done using the standard open aperture Z-scan technique whose signatures together with the optical limiting curves of the samples under investigations in nano seconds (ns) and femto seconds (fs). Also it was found that at lowest value the open aperture transmission curve is symmetric with respect to the focus (z=0) and linear absorption spectra of the compounds have some absorption at the excitation wavelength (532 nm). In the Z-scan curves the symbols indicate experimental data and the solid lines indicate theoretical fit according to the model for SA associated with two photon absorption (2PA).



4.21 Measured NLO parameters of 7'-methyl-4'-phenyl-3-thioxo-1,2,4-triazino quinolin-5-one 18b.

Fig (178) Table 12 Open aperture Z-scan signatures of 7'-methyl-4'-phenyl-3-thioxo-1,2,4triazinoquinolin-5-one18b.

From the **Fig** (178), it was found that the measured nonlinear absorption (NLA) coefficients vary with incident intensity¹⁴. The compound showed the better NLO behaviour which can be attributed to the higher level of electron delocalization due to the presence of more electronegative atoms.

4.22 Measured NLO parameters of 5-phenyl-7-methyl-1,4-trihydro-2*H*-pyridazino[3,4-*b*] quinolin-3-one 26a.

The Z- scan parameters obtained for the compound **26a** were shown in **Table 13(fig179).** All the open aperture Z-scan curve was found to fit well with the NLA mechanism of 2PA assisted exited state absorption. The observed nonlinearity was found to be recognisable.





4.23 Measured NLO parameters of 3-chloro-1-((7-chloro-4-methylquinolin-2-yl) amino)-4-(2-hydroxyphenyl) azetidin-2-one 28



$\boldsymbol{\beta}$ (Non linear optical coefficient)	2.40 x 10 ⁻¹⁰ m/W
I saturation	$80.10 \text{ x } 10^{10} \text{ W/m}^2$
wavelength	532.00nm
omega zero	21.50 microns
Pulse width	7000.00 ps
Average Energy	29.19 mjoule
Slices	1000.00
Linear Transmision	0.69

Fig (180) Table 14 Open aperture Z- scan signatures of 3-chloro-1-((7-chloro-4-methylquinolin-2yl) amino)-4-(2-hydroxyphenyl) azetidin-2-one 28b.

Open aperture **z-scan** traces of the sample curve for the compound **28b** is shown in **Fig (180)**. In this case also the experimental data was found to be fitted well with the equation for 2PA assisted exited state absorption. The compound exhibited considerable nonlinear response.

4.24 Measured NLO parameters of 2-(2-hydroxyphenyl)-3-((2-phenyl quinolin-4-yl) amino) imidazolidin-4-one 37c.



Fig (181) Table 15 Open aperture Z- scan signatures of 2-(2-hydroxyphenyl)-3-((2-phenyl quinolin-4-yl) amino) imidazolidin-4-one 34c.

In the case of compound 34c also the experimental data was found to be fitted well with the equation for 2PA assisted exited state absorption. The compound exhibited significant nonlinear response. 4.25 Measured NLO parameters of 3-((7-methyl-4-phenylquinolin-2-yl) amino) - 2-(2-hydroxyphenyl) thiazolidin-4-one 34b.



Fig (182) Table 16 Open aperture Z- scan signatures of 3-((7-methyl-4-phenylquinolin-2yl)amino)-2-(2-hydroxyphenyl) thiazolidin-4-one 34b.

The normalized open aperture Z-scan traces of the compound **34b** is shown in **Fig** (**182**). It is seen that the transmission is symmetric with respect to the focus (z=0) where it has a minimum in the open aperture signature which reveals TPA or RSA may occur with a positive NLA coefficient β .

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