

A REVIEW ON NONLINEAR OPTICAL PROPERTIES OF DONOR-ACCEPTOR DERIVATIVES OF NAPHTHALENE AND AZANAPHTHALENE

Hamit Alyar

Department of Physics, Faculty of Sciences, Çankırı Karatekin University, TR-18100 Çankırı, Turkey

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Abstract. The nonlinear optical properties of 27 selected donor-acceptor isomeric derivatives of naphthalene, quinoline, quinazoline and triazanaphthalene, including electron donor molecules such as phenyl, aminophenyl, and N, N-dimethylaminophenyl, were discussed and compared with literature values. The theoretical calculations were performed with three different hybrid density functional theories (DFT) *i.e.* BPV86, B3LYP and B3PW91, and 6-311++G(2d,p) basis set was used. The results show that these molecular systems have large first static hyperpolarizabilities. In addition, the NLO response of these molecular systems decreases dramatically when the N, N-dimethylaminophenyl is replaced by aminophenyl or phenyl. This study is extended to the determination of AM1 semi empirical polarizability together with QSAR-quality empirical polarizability using Miller's scheme and molecular volume calculations from optimized geometries using HyperChem v7. Semi empirical AM1 and QSAR-quality empirical polarizability calculations showed poor quantitative agreement with the DFT results, but give excellent statistical correlation coefficients with the DFT values. This implies that the results of such lower calculations can suitably scale for predictive purpose.

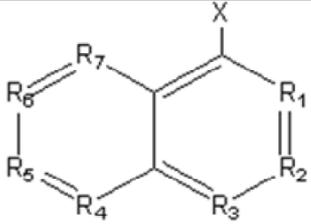
1. INTRODUCTION

Molecular materials with nonlinear optical (NLO) properties are currently attracting considerable attention because of their potential applications in the optoelectronic devices of telecommunications, information storage, optical switching, signal processing [1-5] and terahertz (THz) wave generation [6]. In the last decade, a large range of donor-acceptor substituted compounds have been investigated in order to determine an empirical relationship between molecular structure and nonlinear response. The design of efficient organic materials for applications in nonlinear optical effect is based on asymmetric polarization, induced by electron donor and electron acceptor groups on either side of the molecule at appropriate positions in the molecular systems. By increasing the donor-

acceptor capability of the substitutions attached to the π -conjugated system, nonlinearity can be increased. The position of the substitutions is of vital important in terms of NLO activity. The large value of the first hyperpolarizability, β , which is the measure of the nonlinear optical activity of the molecular system, is associated with intramolecular charge transfer resulting from an electron cloud movement through a π conjugated framework from electron donor to electron acceptor groups.

N, N-dialkylamino groups have higher electron donating character, and there is a long history of theoretical studies on the NLO properties of dialkylamino substitute [7-9]. Herbich et al. synthesized new donor-acceptor naphthalene and azanaphthalene derivatives and reported their intramolecular excited charge transfer states [10].

Corresponding author: Hamit Alyar, e-mail: halyar@karatekin.edu.tr

Table 1. Structures of the D-A naphthalene, quinoline and quinazoline derivatives (containing N,N-dimethylaminophenyl and p-aminophenyl as an electron donor).


X= N,N-dimethylaminophenyl								Name
No	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	R ₇	
1	C	C	C	C	C	C	C	1-(4-Dimethylaminophenyl)naphthalene
2	C	C	N	C	C	C	C	4-(4-Dimethylaminophenyl)quinoline
3	N	C	N	C	C	C	C	4-(4-Dimethylaminophenyl)quinazoline
X= p-aminophenyl								Name
4	C	C	C	C	C	C	C	1-(4-aminophenyl)naphthalene
5	C	C	N	C	C	C	C	4-(4-aminophenyl)quinoline
6	N	C	N	C	C	C	C	4-(4-aminophenyl)quinazoline

The design of new systems with a high charge transfer is a key part of this, because intra molecular charge transfer between donor and acceptor will lead to a very large value for β . The theoretical prediction of accurate electro-optical properties for this kind of system is a very important step towards the rational design of novel nonlinear optical materials. The study of such effects involves the initial determination of static polarizabilities and hyperpolarizabilities in the gas phase. The polarizability of naphthalene has been extensively studied experimentally [11-13] with different theoretical methods and basis sets [14-16]. There do not appear to be any corresponding experimental data in the existing literature, neither are there any other ab initio calculations for title molecules.

Density functional theory (DFT) calculations with various functional are excellent methods in the design of NLO molecules and they help predict properties of the new materials, such as molecular dipole moments, polarizability, and hyperpolarizabilities [17-21]. In earlier studies, the author and other researchers reported the calculation of torsional behaviour and the nonlinear optical properties of 2-, 3-, 4-phenylpyridine [22], phenyltriazines [23] and thalidomide [24] using DFT. In this research, nonlinear optical properties of donor-acceptor isomeric derivatives of naphthalene, quinoline and quinazoline as well as a family of isomeric tri azanaphthalenes containing N, N-dimethylaminophenyl, p-aminophenyl and phenyl as an electron donor were calculated with DFT variants. The studied molecules are presented in Tables 1-4.

The ground state molecular dipole moments (μ_g) and the dihedral angles (θ_{A-D}) (between the planes of the donor and acceptor subunits) of some of the title molecules were calculated with AM1 and ZINDO/S methods by Herbich et al. [10]. A comparison between these results and those of the B3LYP values were performed.

This study is extended to the determination of AM1 [25] semi empirical polarizability together with QSAR-quality empirical polarizability using Miller's scheme and molecular volume calculations from optimized geometries using HyperChem v7 [26].

2. COMPUTATIONAL

The geometries were fully optimized without any constraint with the help of analytical gradient procedure implemented within Gaussian 03W program [27]. All the parameters were allowed to relax and all the calculations converged to an optimized geometry which corresponds to a true energy minimum revealed by the lack of imaginary values in the frequency calculations.

The performance of various DFT functional and of basis sets in hyperpolarizability calculations have been extensively studied for organic NLO materials [28-31]. The nonlinear optical properties of donor-acceptor derivatives of naphthalene and azanaphthalenes were computed for different approximations of exchange and correlations because the quality of approximation might have an important effect in DFT for such hydrogen-bonded systems [32]. The BPV86, which uses Perdew's 1986 functional with local correlation replaced by

Table 2. Structures of the D-A naphthalene, quinoline and quinazoline derivatives (containing N,N-dimethylaminophenyl and p-aminophenyl as an electron donor).

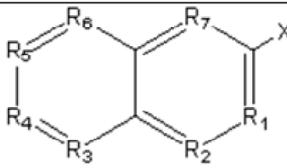
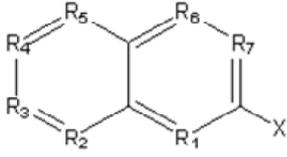
								
X= N,N-dimethylaminophenyl								
No	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	R ₇	Name
7	C	C	C	C	C	C	C	2-(4-Dimethylaminophenyl)naphthalene
8	C	C	C	C	C	C	N	2-(4-Dimethylaminophenyl)quinoline
9	N	C	C	C	C	C	N	2-(4-Dimethylaminophenyl)quinazoline
X= p-aminophenyl								
10	C	C	C	C	C	C	C	2-(4-aminophenyl)naphthalene
11	C	C	C	C	C	C	N	2-(4-aminophenyl)quinoline
12	N	C	C	C	C	C	N	2-(4-aminophenyl)quinazoline

Table 3. Structures of the D-A quinoxaline and isomeric triazanaphthalenes (containing N,N-dimethylaminophenyl and p-aminophenyl as an electron donor).

								
X= N,N-dimethylaminophenyl								
No	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	R ₇	Name
13	N	C	C	C	C	N	C	2-(4-Dimethylaminophenyl)quinoxaline
14	N	N	C	C	C	N	C	N,N-dimethyl-4-(pyrido[3,2-b]pyrazin-3-yl)benzenamine
15	N	C	N	C	C	N	C	N,N-dimethyl-4-(pyrido[4,3-b]pyrazin-3-yl)benzenamine
16	N	C	C	N	C	N	C	N,N-dimethyl-4-(pyrido[3,4-b]pyrazin-2-yl)benzenamine
17	N	C	C	C	N	N	C	N,N-dimethyl-4-(pyrido[2,3-b]pyrazin-2-yl)benzenamine
X= p-aminophenyl								
	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	R ₇	Name
18	N	C	C	C	C	N	C	2-(4-aminophenyl)quinoxaline
19	N	N	C	C	C	N	C	4-(pyrido[3,2-b]pyrazin-3-yl)benzenamine
20	N	C	N	C	C	N	C	4-(pyrido[4,3-b]pyrazin-3-yl)benzenamine
21	N	C	C	N	C	N	C	4-(pyrido[3,4-b]pyrazin-2-yl)benzenamine
22	N	C	C	C	N	N	C	4-(pyrido[2,3-b]pyrazin-2-yl)benzenamine

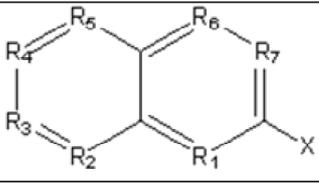
that which was suggested Vosko et al. (VWN)[33-35], Becke's three-parameter exchange functional and the gradient corrected functional of Lee, Yang, and Parr (B3LYP)[33, 36], and Becke's three-parameter functional with Perdew-Wang correlation functional (B3PW91) [33, 36, 37] were used in this study. Accurate calculation of nonlinear optical properties requires the use of extended basis sets and a high level of theory. In particular, these basis sets have to include d and p polarization functions together with s and p diffuse functions. In the present work, the 6-311++G(2d, p) [38-40] basis set was chosen for calculation of static polarizability,

anisotropy of polarizability and first static hyperpolarizability.

AM1 semi empirical calculations were performed with HyperChem v7. Also, molecular volume, and the Miller-Savchik polarizability were found from optimized MM+ geometries using HyperChem v7. All statistical analyses were performed with SPSS software v.13.0 (SPSS Inc., Madrid, Spain) [41].

3. RESULTS AND DISCUSSION

Firstly, it would be productive to discuss the general properties of geometry. Borbulevych et al. studied

Table 4. Structures of the D-A quinoxaline and isomeric triazanaphthalenes (containing phenyl as an electron donor).


X= phenyl

No	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	R ₇	Name
23	N	C	C	C	C	N	C	2-phenylquinoxaline
24	N	N	C	C	C	N	C	3-phenylpyrido[3,2-b]pyrazine
25	N	C	N	C	C	N	C	3-phenylpyrido[4,3-b]pyrazine
26	N	C	C	N	C	N	C	2-phenylpyrido[3,4-b]pyrazine
27	N	C	C	C	N	N	C	2-phenylpyrido[2,3-b]pyrazine

Table 5. Results of B3LYP and AM1 semiempirical calculations for title molecules: μ_g , ground state dipole moments; (Θ_{A-D}), angles between the planes of donor and acceptor subunits which are related to the equilibrated ground-state conformation of the molecule; E_{H-L} , molecular orbital energy difference.

Molecule	E/a.u.		μ_g/D		Θ_{A-D}°		E_{H-L}/eV
	B3LYP	B3LYP	AM1(Ref.10)	ZINDO/S(Ref.10)	B3LYP	AM1	B3LYP
1	-751.11995	2.78	1.9	1.7	59.1	57	4.06
2	-751.12409	2.93	1.9	2.0	36.2	38	3.95
3	-767.16524	5.63	3.3	4.6	54.2	56	3.91
4	-672.49087	1.65			59.8		4.28
5	-672.49575	2.21			56.4		4.18
6	-688.53491	4.32			42.5		4.09
7	-767.17160	3.07	2.4	3.8	36.2	39	3.69
8	-783.21378	6.02	3.9	4.7	17.4	57	3.65
9	-783.21946	1.33	1.2	2.0	0.0	35	3.42
10	-688.54324	2.36			37.7		3.94
11	-704.58115	4.56			17.7		3.93
12	-704.59131	1.21			0.0		3.69
13	-783.21188	4.13	2.4	2.8	16.5	37	3.43
14	-799.25367	4.26	2.8	2.9	10.9	36	3.25
15	-799.25095	6.63	4.2	5.6	16.2	37	3.28
16	-799.25137	7.61	4.9	6.4	14.9	37	3.33
17	-799.25327	6.28	4.3	5.2	16.8	37	3.28
18	-704.58218	2.87			19.2		3.69
19	-720.62499	3.41			13.9		3.51
20	-720.62219	5.59			18.3		3.54
21	-720.62202	6.32			17.3		3.62
22	-720.62212	4.72			18.7		3.53
23	-649.20304	0.45			25.1		4.26
24	-665.24447	1.91			22.2		4.18
25	-665.24163	3.11			24.9		4.16
26	-665.24130	3.51			24.6		4.34
27	-665.24449	3.32			24.9		4.19

the 13 relevant compounds with the N,N-dimethyl-4-nitroaniline fragment taken from the Cambridge Structural Data base. Their study demonstrated that there are significant differences in the structure of these compounds related to the geometry of the dimethylamino group. These compounds may be divided into two groups: the first group, the dimethylamino group, is planar and coplanar or rotated with respect to the benzene ring; the second

group of compounds has a trigonal-pyramidal configuration and is twisted with respect to the ring [9]. In the present study, configuration of the NH_2 and dimethylamino fragments are in a pyramidal configuration but not twisted with respect to the benzene ring.

Theoretically, the torsional angles (Θ_{A-D}) between the planes of the donor and acceptor subunits and dipole moments of title molecules was previously

Table 6. Polarizability calculations for naphthalene (table values are in atomic units (a.u.)).

Basis Set	α_{xx}	α_{yy}	α_{zz}	$\langle\alpha\rangle$
^a HF/6311++G(3d,2p)	65.62	116.35	157.95	113.31
^b HF/6-31G(d,p)	33.03	104.68	142.98	93.56
^b HF/6-31+G	57.69	110.00	149.99	105.89
^b HF/6-31+G(d,p)	60.95	112.20	153.69	108.95
^b HF/6-31+G(3d,3p)	65.82	116.84	159.29	113.98
^c HF/Spackman	63.20	121.40	163.90	116.20
^c B3LYP/Spackman	62.20	125.90	172.10	120.10
^a BLYP/6-311++G(3d,2p)	65.72	123.93	170.47	120.04
B3LYP/6-311++G(2d,p)	63.72	121.82	167.77	117.81
B3PW91/6-311++G(2d,p)	62.27	120.97	166.65	116.63
BPV86/6-311++G(2d,p)	63.61	123.60	171.69	119.63
^d Exp.				117.40

^aFrom Ref.11, ^bFrom Ref.12, ^cFrom Ref.13, ^dFrom Ref. 8

reported using semi empirical AM1 and ZINDO/S methods [10]. All previous and B3LYP results are presented in Table 5. AM1 Θ_{A-D} values are compatible with B3LYP for (1-3) and (7) molecules, although for (8,9) and (13-17) they are not compatible. The differences between B3LYP values and those reported by Herbich et al. can be interpreted in terms of the employed density functional approach.

It is well known that the nonlinear optical response of an isolated molecule in an electric field E_j can be presented as a Taylor series expansion of the total dipole moment, μ_{tot} , induced by the field:

$$\mu_{tot} = \mu_0 + \alpha_{ij} E_j + B_{ijk} E_j E_k + \dots,$$

where α is the linear polarizability, μ_0 the permanent dipole moment and β is the first hyperpolarizability tensor components. The isotropic (or average) linear polarizability and anisotropy of polarizability is defined as [42]:

$$\langle\alpha\rangle = 1/3(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}),$$

$$\Delta\alpha = 1/2\left[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{xx} - \alpha_{zz})^2 + (\alpha_{yy} - \alpha_{zz})^2\right]^{1/2}.$$

The complete equation for calculating the total static first hyperpolarizability magnitude of Gaussian output is given as follows [43],

$$\beta_{tot} = \left[(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2\right]^{1/2}.$$

Polarizability of naphthalene with different methods and basis sets were previously studied by Hincliffe et al. [14,15] and Howard et al.[16]. In the present study, the polarizability of naphthalene was also calculated with BPV86, B3LYP and B3PW91

methods and 6-311++G(2d,p) basis set. Naphthalene has a center of symmetry so its first hyperpolarizability is zero by symmetry. All calculated and experimental polarizability values are presented in Table 6.

As can be seen from Table 6, the B3LYP and B3PW91 mean polarizability values are closer to the experimental values than other methods. Therefore, the DFT methods and the 6-311++G(2d,p) basis set were selected for the current calculations. The calculated static mean polarizabilities, anisotropy of polarizabilities and total first hyperpolarizabilities of the studied compounds (1-27) are listed in Table 7.

The discussion will be focused mostly on the first hyperpolarizability because the main objective of this work is to describe a general mechanism for obtaining large first-order optical nonlinearities in substituted naphthalene and azanaphthalene derivatives.

In particular, the results of the calculations showed that the magnitudes of hyperpolarizabilities are mainly dependent on the degree of the δ electron delocalization in the aniline rings. Optical response properties are governed by the increasing of both conjugation length and strength of donor and acceptor groups. Also, the nitrogen numbers and positions on the naphthalene are very important for nonlinearity of the title molecules.

The 3D plots of important molecular orbital are shown in Fig. 1 for compound (14). The frontier molecular orbitals play an important role in the electronic and optical properties, as well as in UV-vis spectra and chemical reactions [44]. Also, the energy gap between HOMO and LUMO is a critical parameter in determining molecular electrical transport properties and an electronic system with a larger HOMO-LUMO gap should be less reactive than with a smaller gap [45]. The energy gap of HOMO-LUMO explains the eventual charge transfer

Table 7. Results of static polarizability ($\langle\alpha_{ave}\rangle$); anisotropy of polarizability ($\Delta\alpha$) and first static hyperpolarizability (β_{tot}) for studied molecules.

Molecule	$\langle\alpha\rangle$ /a.u.			$\Delta\alpha$ /a.u.			β_{tot} /a.u.			
	AM1	BPV86	B3PW91	B3LYP	BPV86	B3PW91	B3LYP	BPV86	B3PW91	B3LYP
1	173.01	246.20	236.56	238.57	124.83	115.40	114.91	2866.8	1896.2	1856.8
2	208.11	244.37	233.52	235.38	132.58	120.58	120.12	4611.9	2984.4	2902.1
3	170.09	248.27	235.23	236.95	157.43	140.80	140.32	7341.9	5092.6	5044.1
4	164.18	212.75	204.73	206.24	104.86	96.70	97.82	1705.6	1129.5	1080.4
5	160.18	209.11	201.02	202.81	107.98	99.74	99.65	2557.0	1747.8	1735.0
6	156.29	210.48	201.00	202.49	127.02	115.84	115.58	4299.3	3082.1	3098.8
7	192.32	268.56	252.40	254.40	204.74	180.45	180.01	6046.5	4032.4	3958.1
8	193.11	269.70	254.84	256.75	217.29	195.83	195.39	8728.2	6228.6	6167.2
9	192.98	268.37	252.36	254.16	227.07	202.84	202.44	10509.1	7682.5	7654.8
10	175.26	227.36	217.70	220.09	167.44	154.56	154.70	3576.2	2540.9	2547.1
11	171.42	229.92	218.76	220.55	181.90	166.27	166.22	5355.4	3941.5	3971.1
12	169.02	227.42	215.39	217.12	188.71	171.00	171.05	6626.1	5130.9	5059.5
13	194.56	269.32	253.68	255.44	22.81	204.76	204.31	10075.5	7255.2	7197.9
14	191.17	269.85	253.01	254.66	240.18	214.11	213.67	12842.8	9519.3	9494.5
15	191.32	264.30	248.18	249.82	228.00	203.45	203.06	10811.7	7929.9	7827.7
16	189.32	266.06	249.78	251.39	230.17	205.46	204.56	11642.9	8834.6	8791.5
17	187.79	266.57	250.06	251.71	232.29	207.14	206.68	12055.7	8617.3	8570.6
18	170.48	228.17	216.54	218.26	189.01	172.31	172.33	6066.1	4477.2	4513.4
19	167.03	226.83	214.44	216.06	196.87	178.44	178.53	7952.4	6000.6	6074.2
20	167.10	248.41	210.49	212.10	157.70	169.44	169.54	7341.9	4837.8	4888.1
21	165.08	223.51	211.44	213.04	187.70	170.13	170.18	7174.8	5527.0	5568.0
22	162.70	224.32	212.20	213.83	190.84	173.13	173.18	7312.6	5354.0	5408.5
23	150.11	204.28	193.17	194.92	150.60	136.43	136.69	972.0	631.9	646.7
24	147.27	196.16	188.78	190.43	146.72	137.69	138.00	1901.4	1415.0	1450.6
25	148.56	193.49	186.19	187.82	140.23	131.44	131.72	1184.5	825.0	847.7
26	146.74	193.35	186.19	187.67	138.48	131.43	130.08	16562	1241.4	1258.0
27	149.08	198.73	187.69	189.33	148.93	134.83	135.11	1654.5	1106.6	1131.7

interaction within the molecule. In this study, the frontier orbital energy gap for compound (14) is found to be 3.25 eV by B3LYP method.

As a result of the calculations we have made, findings obtained from Tables 1-7 are as follows:

(i) Polarizability calculations with 6-311++G(2d,p) basis set for naphthalene are very closer to experimental value than the results of the other studies [11-13].

(ii) As can be seen from the comparison of data collected in Table 6, the B3LYP calculated dipole moment of studied molecules are higher in comparison with that predicted at the semi-empirical AM1 and ZINDO/S methods [10] due to the DFT includes correlation effects.

(iii) The largest β_{tot} values are expected for the isomeric tri azanaphthalenes (14-17) due to the N,N-dimethylaminophenyl as an electron donor with three nitrogen atoms on the naphthalene rings.

(iv) The B3PW91 method calculates the polarizabilities approximately one percent lower than B3LYP. However, this method calculates one percent larger hyperpolarizability compare to the B3LYP. BPV86 polarizability, anisotropy of polarizability, and first static hyperpolarizability calculations are in poor quantitative agreement with the B3LYP and

B3PW91 results; the differences are approximately 3-6 % for $\langle\alpha\rangle$, 30-60 % for β_{tot} .

(v) The phenyl and p-aminophenyl substitution on the isomeric D-A naphthalene, quinoline, quinazoline, quinoxaline and tri azanaphthalene derivatives (containing N,N-dimethylaminophenyl as an electron donor) decreased the β_{tot} by between 6.5-10% and 1.56-1.70% respectively due to N,N-dimethylaminophenyl electron donor group being stronger than the phenyl or aminophenyl groups.

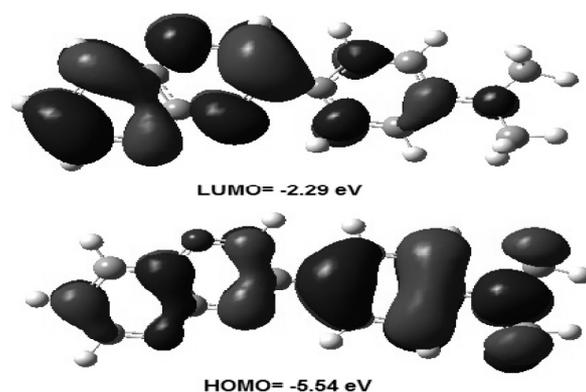


Fig. 1. Molecular orbital electron density of compound.

Table 8. Various quantities for derivatives of the naphthalene and azanaphthalene.

No.	Volume (Å ³)	Miller (Å ³)
1	789.69	32.38
2	787.42	32.38
3	706.91	31.68
4	635.63	25.24
5	699.42	28.71
6	702.74	28.71
7	786.43	31.68
8	781.32	30.97
9	784.93	30.97
10	695.19	28.01
11	670.87	27.30
12	688.68	27.30
13	782.88	30.97
14	769.82	30.26
15	767.35	30.26
16	768.02	30.26
17	771.61	30.26
18	684.05	27.30
19	670.29	26.59
20	670.13	26.59
21	670.46	26.59
22	661.13	26.59
23	641.53	25.95
24	631.31	25.24
25	635.08	25.24
26	634.71	25.24
27	635.63	25.24

(vi) β_{tot} of (1-3) molecules vary according to nitrogen atom numbers on the naphthalene as $\beta_3 > \beta_2 > \beta_1$ ordered. The same trend was observed for (4-6) molecules (as $\beta_6 > \beta_5 > \beta_4$).

(vii) When N,N-dimethylaminophenyl going from position 1 to 2 as in the Tables 1-2, β_{tot} are increased by c.a. 100% for (7,8) and c.a. 50% for (9). The same trend was observed for (10-12) molecules. However, on comparison of compound (1) with (7), the resonance of the molecule seems different regarding the π electrons localized in the nitrogen atom in compound (1) but not in compound (2). The case increased the hyperpolarizability in compound (2). The trend could be the same for compounds (2), (8) and compounds (3), (9) (see Table 7). When the negative formal charge is on the N atoms, then the push-pull effect is larger. Similarly, the increase of hyperpolarizability when N,N-dimethylaminophenyl going from position 1 to 2 results in the steric effect between diaminophenyl and naphthalene, quinoline, quinazoline and quinoxaline groups, the steric effect at position 1 is larger than 2.

(viii) The hyperpolarizability of (13-22) molecules in the compounds is the highest, which have three

nitrogen atoms in the aromatic ring and two of them in the same location in space may affect the unbounded electrons and make the largest hyperpolarizability. Although (23-27) molecules have three nitrogen atoms in the same location, hyperpolarizability of them lower than (13-22) molecules due to the molecules have different X donor groups. Strong donor and acceptor groups have vital importance in determining the new systems which have large hyperpolarizability. Intra molecular charge transfer between donor and acceptor will lead to a very large value for β .

(ix) The lowest β_{tot} values were calculated for (13) among (13-17) due to the nitrogen number being two on the naphthalene for molecule (13) and three for molecules (14-17).

(x) It was found that first static hyperpolarizability of compound (14) is 12842.8 a.u., the largest value for the studied molecules.

(xi) It can be seen that from Table 5 and 7, first static hyperpolarizability and optical band gap (E_{H-L}) is inverse relationship for the same molecule groups.

3.1. QSAR-quality calculations

Dipole polarizability is often used in QSAR studies, where the aim is to give a reliable but quick estimate of $\langle \alpha \rangle$. DFT polarizability calculations are prohibitively expensive in a QSAR context, even for such simple molecules. One therefore looks to less rigorous but reliable procedures.

The relationship mean polarizability and molecular volume (V_{mol}) is defined as [14];

$$\langle \alpha \rangle = 4\pi\epsilon_0 V_{\text{mol}}$$

The molecular volume can be estimated very easily from molecular mechanics without the cost of a full quantum mechanical calculation. The molecular volumes are routinely determined in QSAR studies, and typical values are shown in Table 8 with Miller $\langle \alpha \rangle_{\text{Miller}}$ empirical polarizability.

Whilst the quantitative agreement with Miller $\langle \alpha \rangle_{\text{Miller}}$ empirical polarizability values and B3LYP ones are clearly nonexistent, there is a good least square fit for the two sets of data, with a correlation coefficient of 0.91. The correlation coefficient was found to be 0.95 between the molecular volumes and B3LYP mean polarizability.

The AM1 mean polarizability calculations give values that correlate well with the B3LYP (with a correlation coefficient of 0.95).

Finally, DFT polarizability calculations at B3LYP/6-311++G(2d,p) level of theory are adequate for these

Table 9. Linear regression coefficients R for the derivatives of naphthalene and azanaphthalene.

Correlation of $\langle\alpha\rangle$ B3LYP with	
Molecular volume	$R = \langle\alpha\rangle \text{ B3LYP} = 0.952$ ($Y = 0.399X + 15.477$)
$\langle\alpha\rangle$ Miller	$R = \langle\alpha\rangle \text{ B3LYP} = 0.907$ ($Y = 9.150X + 10.746$)
$\langle\alpha\rangle$ AM1	$R = \langle\alpha\rangle \text{ B3LYP} = 0.955$ ($Y = 1.379X + 16.116$)
$\langle\alpha\rangle$ B3PW91	$R = \langle\alpha\rangle \text{ B3LYP} = 0.953$ ($Y = 0.960X + 15.711$)
$\langle\alpha\rangle$ BPV86	$R = \langle\alpha\rangle \text{ B3LYP} = 0.958$ ($Y = 1.0908X - 9.0122$)

complex molecules. However, we consider the likely reliability of various easily-computed indices, such as the molecular volume, the Miller empirical volume polarizabilities, and AM1 polarizabilities discussed above. According to obtained results of linear regression, the coefficients are given in Table 9.

5. CONCLUSION

In this research, nonlinear optical properties of 27 selected donor-acceptor isomeric derivatives of naphthalene, quinoline, quinazoline and triazanaphthalene were studied and some of the values obtained from the present study were compared with literature values. AM1 Θ_{A-D} values are compatible with B3LYP for (1-3) and (7) molecules, although (8, 9) and (13-17) are not compatible due to the use of different methods.

First static hyperpolarizability of these compounds was affected by the position of donor moieties and the number of nitrogen atoms on the naphthalene. The larger β_{tot} values were obtained for the isomeric tri azanaphthalenes (14-17) due to the N,N-dimethylaminophenyl being a stronger electron donor than the others with three nitrogen atoms on the naphthalene rings. It was found that first static hyperpolarizability of the compound (14) with the BPV86 method is 12842.8 a.u., the largest value for the studied molecules. Besides, it was found that first static hyperpolarizability and optical band gap (E_{H-L}) is inverse relationship for the same molecule group.

The results of this study show that these molecular systems have large first static hyperpolarizabilities and may have potential applications in the development of NLO materials.

Semi-empirical polarizability at the AM1 level of theory can be considered together with QSAR-quality empirical polarizability calculations using Miller's scheme. Least-squares correlations between the various sets of results show that these less costly procedures are reliable predictors of $\langle\alpha\rangle$ for the title molecules, but less reliable for the larger molecules. It can be seen from the results that there are good correlations with the DFT results and those given by cheaper procedures, such as calculated

molecular volume, and the Miller empirical polarizability, and semi empirical models, such as AM1.

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