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Research Article

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Characterization and Computational analysis of unsymmetrical azines

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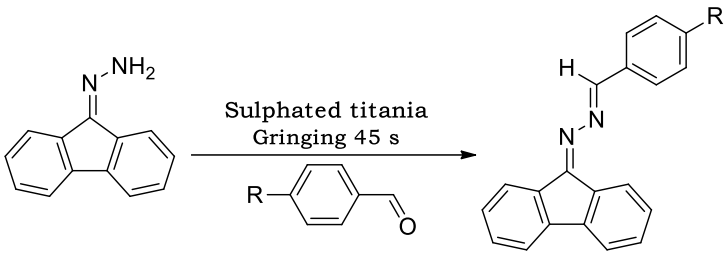
Abstract: Unsymmetrical azines **(1–6)** were prepared by sulphated titania and characterized by FT-IR, ^{1}H and ^{13}C NMR spectral studies. Nonlinear optical (NLO) behavior of the unsymmetrical azines is explained by the theoretically observed values of dipole moment (μ), polarizability (α_0) and first hyperpolarizability (β_{tot}). The natural bond orbital (NBO) analysis of the unsymmetrical azines are made using B3LYP/6-31+G (d,p) basis set. Frontier molecular orbital are also performed for the azines.

Keywords: unsymmetrical azines, sulphated titania, NLO, NBO, solvent-less.

1. INTRODUCTION

Azines, N–N linked diimines are having great application in synthetic organic chemistry and have interesting reactions and applications [1]. Azines have been formed use as antimicrobial drugs [2], pigments and dyes [3,4], liquid crystals [5] etc. Recently Ortiz *et al.* [6] have been reported azine contain oligothiophene-based oligomeric and polymeric semiconductors to be used in the field–effect transistor applications. Jedryka *et al.* [7] revealed symmetrical and unsymmetrical azines as organic photovoltaic applications. Several methods have been proposed for the synthesis of azines such as thermal, microwave irradiation [8], using catalyst such as $FeCl_3.6H_2O$ [9], nanocrystalline alumina powder [10] and solid hydrazine [11]. Recently Krishnakumar *et al.* [12] have reported the synthesis of azine using sulphated titania acid catalyst. The research of computational methods has resulted in the applications like (i) modeling of drug design (ii) functional material design etc. Most important properties of molecule such as chemical, physical and biological can be predicted by using computational techniques [13]. Nowadays, density functional theory (DFT) has been significant in theoretical analysis. DFT as developed by the great contributions of Kohn, Parr, March and Gross among many others spanning both the quantum physical and chemical communities. It was originally designed to model electronic correlations in solid states and was even applied to superconductivity [14]. Recent scientific articles reveal molecular properties of organic molecules [15-18]. The current investigation is focused on the synthesis of unsymmetrical azines using sulphated titania and its characterized by IR, ^{1}H and ^{13}C NMR spectral studies. The improvement of the work some defect not found in this method such as low yield, using solvents both reaction and purification. The nonlinear optical, natural bond orbital, frontier molecular

orbital were analyzed for the unsymmetrical azines by using B3LYP/6-31+G (d,p) basic set in Gaussian 03 program. The theoretically observed values are discussed, which are answerable for molecular properties of all the synthesized unsymmetrical azines.



Scheme 1.

2. EXPERIMENTAL

2.1 Instruments

FT-IR spectra were recorded using an Avatar-330 FT-IR spectrophotometer using KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on a BRUKER AVANCE^{III} 400 MHz instrument. Computational analysis have been using carried out by Gaussian 03 program.

2.2. Preparation of sulfate loaded TiO_2 acid catalyst

About 12.5 mL of titanium isopropoxide was dissolved in 100 mL of 2-propanol and to this solution 3.2 mL of 1 M H_2SO_4 was added drop wise under vigorous stirring. The resulting colloidal suspension was stirred for 3 h. The gel obtained, it was filtered, washed and dried in an air oven at 100 ^{o}C for 12 h. Addition of barium chloride to the filtrate gave no precipitate indicating that all the sulfate ions were completely loaded on the gel. The sample was calcinated at 400 ^{o}C in a muffle furnace for 3 h [12].

2.3. Preparation of 2-benzylidene-1-(9*H*-fluoren-9-ylidene)hydrazine (1 to 6)

To a mixture of fluorenone hydrazone (1 mmol) and benzaldehyde (1 mmol) in dry condition, 0.1 g of TiO_2-$SO4^{2-}$ was added and the mixture was ground in a mortar with a pestle at room temperature for 45 s. Completion of the reaction was tested by Thin Layer Chromatography (TLC). After completion of the reaction, ethyl acetate was added to the solidified mixture and the insoluble catalyst was separated by filtration. The solvent was evaporated to get the product. The crude sample was recrystallized from absolute ethanol. The structures of azines are established by FT-IR, ^{1}H and ^{13}C NMR analysis.

2.4 2-benzylidene-1-(9H-fluoren-9-ylidene) hydrazine (1)

(Yield=98%); IR (KBr) (cm^{-1}): 1641 (C=N stretching), 3018 (CH), 1086 (N–N); ^{1}H NMR ($CDCl_3$, 400 MHz) (δ, ppm): azomethine proton 8.56. (s, 1H), aromatic protons 7.23−8.46 (13 H). ^{13}C NMR ($CDCl_3$, 100MHz, ppm) = 159.6 (azomethene carbon), 160.4 (imino carbon), ipso carbon signals at 142.5, 141.6, 136.8, 134.4, 133.7 other aromatic carbon signals 131.73–119.90.

2.5 Computational method

Geometry optimization were carried out according to DFT using B3LYP/6-31+G (d,p) basic set available in Gaussian 03 [19] package for azine **1 – 6**. NLO optical behavior of the unsymmetrical azine was also examined theoretically by using B3LYP/6-31G (d,p) method. Frontier molecular orbital analysis (HOMO-LUMO) was also carried by the same method.

3. RESULTS AND DISCUSSION

3.1 Electric moments analysis

NLO is at the lead to modern research because of its importance in providing the key functions like optical modulation, frequency shifting, optical switching, optical logic, and optical memory for the originating technologies in areas such as telecommunications, signal processing, and optical interconnections [20–23]. The total static dipole moment (μ), polarizability (α_0) and hyperpolarizability (β_{tot}) a was calculated using B3LYP/6-31+G (d,p) basis set on the basis of the finite–field approach. In **Table 1** indicate μ values of azines **1 - 6**, azine **3** (1.2079 Debye) and **5** (0.2401 Debye) have more and less dipole moment. Polarizability (α_0) and the first hyperpolarizability (β_{tot}) of molecular system is dependent on the efficiency of electronic communication between acceptor and the donor groups as that will be the key to intra molecular charge transfer [24,25]. The polarizability is a measure of the answer of the outer shell electrons toward an external perturbation. Chemical binding also can be viewed as resulting from reorganization and redistribution of the outermost electron density of atoms due to mutual perturbation, when different atoms are brought closer. In **Table 2**, azine **4** has higher polarizability when compared to all other synthesized azines. **Table 3** shows that azine **1** in the β (xyz) = (99.58929 × 10^{-33}esu), azine **2** β (xyz) = (145.1389 × 10^{-33}esu), azine **3** β (yzz) = (20.41203 × 10^{-33}esu), azine **4** in β (xxx) = (4644.516 × 10^{-33}esu), azine **5** β (xxy) = (1251.796 × 10^{-33}esu) and azine **6** β(xyy) = (240.6322 × 10^{-33}esu) directions are largest values of hyperpolarizability are noticed, and subsequently, delocalization of the electron cloud is much more in that direction [26]. The calculated first hyperpolarizability of azine **1 – 6** is 5.3934, 12.1334, 25.9292, 44.0031, 25.2281 and 11.9328 x10^{-30}esu, which are 14, 32, 70, 118, 68 and 32 times that of urea. We conclude that the all azines are smart object for future studies of non-linear optical properties. Compared β_0 values of **azine 1** (without substitution) and **2** (Methyl), **2** is higher than that of azine **1**. In **azine 2**, the CH_3 group on the benzene ring attributes the electron donating ability of organic segment, so the charge transfer is stronger than that of azine **1** [27].

Table 1. Dipole moment analysis of azine **1–6**

Azines	Dipole moment (μ) Debye			
	μ_x	μ_y	μ_z	μ_{tot}
1	0.256419	-0.00403	-0.72409	0.768158
2	0.558819	0.109633	-0.79759	0.980027
3	0.51003	0.583635	0.926482	1.207944
4	-0.88603	-0.35187	-0.57853	1.115152
5	-0.20233	0.129412	0	0.240173
6	-0.34833	-0.12305	-0.00021	0.369429

Table 2. Polarizability values of azine **1–6**

Parameters	Azines					
	1	2	3	4	5	6
α_{xx}	393.0613	413.8452	423.3201	485.7868	427.697	392.1979
α_{xy}	-9.25997	-9.70691	-9.61805	5.791353	-93.7061	-3.54597
α_{yy}	299.6768	313.5677	324.5176	330.9301	321.8431	274.3292
α_{xz}	18.06696	24.22523	-28.4659	-25.4067	0	0.018709
α_{yz}	-6.65383	-4.29691	1.256835	-4.65257	0	-0.00427
α_{zz}	157.2344	171.9247	176.7747	187.6324	53.84412	50.80567
(α)	0.7451	0.7847	0.8067	0.8792	0.7674	0.6834

3.2 Frontier molecular orbital analysis (HOMO–LUMO)

The frontier molecular orbitals (HOMO and LUMO) and frontier orbital gap (band gap) helps to exemplify the chemical reactivity and kinetic stability of the molecules, and are important parameters for quantum chemistry [28]. The band gaps in conjugated azines are governed by their chemical structures. Therefore, the detailed band gap theoretical calculations were carried out by using B3LYP/6-31+G (d,p) level. The band gap can sometimes serve as a measure of the excitability of the molecule, smaller the energy; the more easily a molecule's electrons will be excited. The HOMO–LUMO energy gap is an important stability index and a large energy gap implies high stability for the molecule. Therefore **azine 4** (Eg = 2. 5864 eV) characterizes the highest stability when compared to other azines. Lower HOMO-LUMO energy gap **azine 6** will be exceptionally easy to reduce and quite amenable for use as an organic semiconductor [29] and further application, lower in the HOMO–LUMO energy gap explicates the (i) intramolecular charge transfer must occur within the molecule and (ii) eventual charge transfer interaction place within the molecule, which are answerable for the bioactive property of the biomedical compound (-**SCH_3** substituted azine may possible to bioactive compounds) [30]. HOMO-LUMO shapes and band gap of azines are shown in **Fig 1-3 (a and b)**.

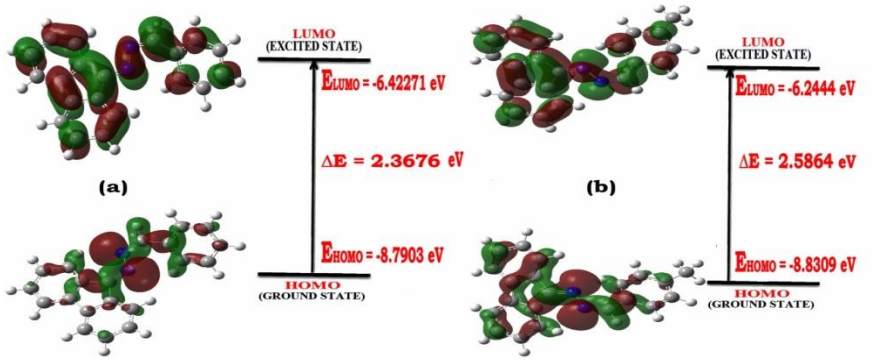


Figure 1. (a) HOMO - LUMO energy gap for azine 1 (b) for azine 2

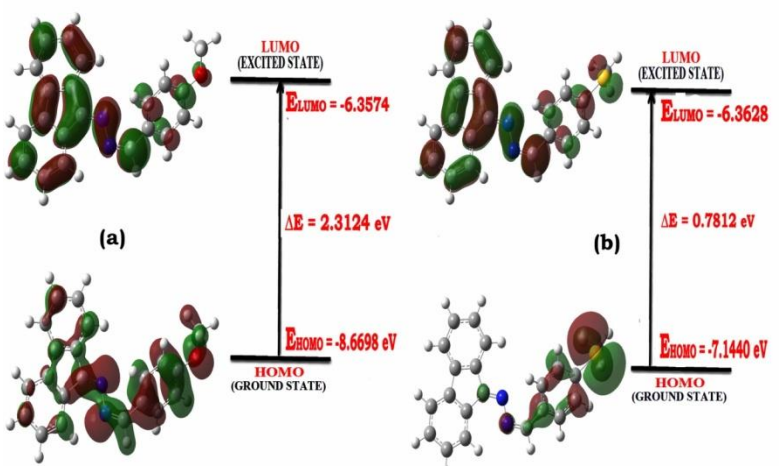


Figure 2. (a) HOMO - LUMO energy gap for azine 3 (b) for azine 4

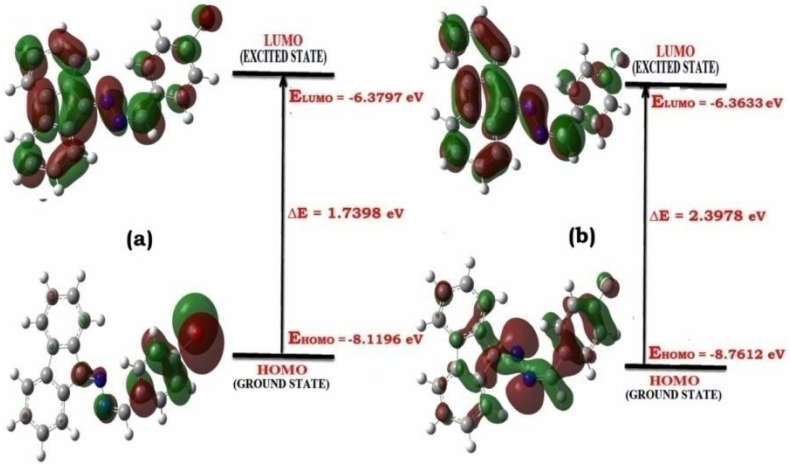


Figure 3. (a) HOMO - LUMO energy gap for azine 5 (b) for azine 6

Table 3. Second Order Perturbation theory analysis of fock matrix in NBO azines **1–6**.

Parameters	Azines					
	1	2	3	4	5	6
β_{xxx}	-638.187	-1265.02	-2685.98	4644.516	-1962.35	-1582.13
β_{xxy}	-76.4569	-172.936	-356.952	-765.404	1251.796	-199.902
β_{xyy}	93.72407	11.81976	-83.5663	95.29923	-484.836	240.6322
β_{yyy}	0.174203	-28.4447	-16.45	-34.646	338.6665	-150.875
β_{xxz}	-87.7762	21.28532	-248.259	602.3324	0	0.048423
β_{xyz}	99.58929	145.1389	-207.029	-291.723	0	0.087103
β_{yyz}	42.65398	28.44163	-33.1473	58.94641	0	0.030151
B_{xzz}	-68.089	-136.636	-198.209	252.879	-0.4994	5.066351
B_{yzz}	-6.45782	5.306504	20.41203	11.05098	2.06752	1.860316
B_{zzz}	-42.5025	-0.89901	6.257458	-34.4229	0	-0.00463
(β_{tot})	5.3934	12.1334	25.9292	44.0031	25.2281	11.9328

3.3 Natural bond orbital analysis (NBO)

NBO analysis is a successful tool for studying interactions in both filled and effective orbital spaces that could enhance the analysis of intra and intermolecular interactions and it also provides a commodious basis for investigating charge transfer or conjugative interaction (hyper conjugation) in molecular systems. NBO have been executed on the azines compounds **1 to 6** at the B3LYP/6-31+G (d,p) level. **Table 3** presented values for the donor–acceptor interactions of azines **1 to 6**. Higher the E (2) value, the more intense the interaction between electron acceptors and electron donors, i.e. the more donating affinity from electron acceptors to electron donors and the greater the extent of conjugation of the entire systems. For each donor (i) and acceptor (j), the stabilization energy E (2) associated with the delocalization i→j is estimated as $E(2) = \Delta E_{ij} = qi\,(F(i,j)^2 / \varepsilon i - \varepsilon j)$ here qi is the donor orbital occupancy, εi and εj are diagonal elements and F (i, j) is the off diagonal NBO Fock matrix element. The second-order perturbation energy E (2) establishes an approximate strength of these delocalization interactions. The highest interactions azines **1-6** are (n -π*) [LP (1) C9 BD*(2) C7-C8] , (π -π*) [BD (2) C5- C6 to BD*(2) C4-C9], (π -π*) [BD (2) C26-C29 to BD*(2) C25-C28], (π -π*) [BD (2) C26-C30 to BD*(2) C25-C27], (π -π*) [BD (2) C17-C23 to BD*(2) C21-C22], (π -π*) [BD (2) C28-C29 to BD*(2) C26-C30] reveal greater stabilization energies [272.92, 96.40, 97.99, 87.07, 90.17, 101.80 kJ mol-1 in that order]. The greater and lower interaction is found in the azines **1** and **4**.

4. CONCLUSION

In this paper, a series of fluorenone azines synthesized by solvent less approach using sulphated titania acid catalyst. In this method operates with great advantages such as low reaction time, high yield, no baleful solvents and simply operation. Synthesized azines have been characterized by IR, ^{1}H and ^{13}C NMR spectral studies. Molecular properties of azines analysis have been done by using Gaussian-03: B3LYP/6-311+G (d,p) basic set. The analysis reveals, (i) azine 3 and 5 have more and less dipole moment (ii) **azine 4** has great polarizability values (iii) first hyperpolarizability of **azine 4** is 44.0031x10-30 esu, which is 118 times greater of urea finally **azine 4** has higher stability when compared all the azines.

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The authors declare no conflict of interest

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