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Synthesis, conformational and theoretical studies of 1,*n*-di(2-formyl-4-phenylazophenoxy)alkanes

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ABSTRACT

1,*n*-di(2-Formyl-4-phenylazophenoxy)alkanes 1 and 2 and 1,3-di(2-formyl-4-phenylazophenoxymethyl) benzene 3 were synthesis and characterized by FT-IR, UV-Vis, ¹H, ¹³C NMR and mass spectral studies. The stable conformations of 1-3 were predicted theoretically and selected geometrical parameters were derived from optimized structures. The molecular parameters of HOMO-LUMO energies, polarizability, hyperpolarizability, natural bond orbital (NBO), atom in molecule (AIM) analysis and molecular electrostatic potential (MEP) surfaces were determined by the density functional theory (DFT) method and analysed.

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1. Introduction

Azobenzene dyes have long been investigated because of their interesting *cis-trans* photoisomerization phenomena [1–4]. The dynamics of cis-trans photoisomerization and configuration of azochromophores has been the target of many studies [5,6]. Azoaromatic derivatives cover a wide variety of compounds which main structural characteristic is the presence of an azo group (-N= N–) connecting two phenyl rings (Ph–N=N–Ph). The attachment of electron donor and/or acceptor groups in different positions of the phenyl rings can shift the absorption and emission bands of these compounds to the visible region. This effect is highly dependent on the solvent [7-10]. Azo compounds can be affected by the solvent properties and temperature changes [11]. Bearing in mind that the trans isomer is the most stable conformation in the absence of steric hindrance, the temperature dependence suggests that torsional changes in the azoaromatic compound structure affects their electronic delocalization, thus, their optical properties. The oxidation-reduction behaviour of these compounds play an important role in their biological activity [12]. The pharmaceutical importance of compounds containing an arylazo group have been

expressed as the value first order molecular hyperpolarizability β , along with a fair good photo- and thermal stability and a good solubility are required molecular. Typically, second order NLO chromophores are constituted by an electron acceptor moiety linked to an electron donor group through a conjugation bridge that allows a charge transfer of π -electrons. Both the strength of the electron donor and acceptor groups and the nature of the conjugation bridge are important parameters in defining the activity of the chromophore. Recently, we have synthesized and determined the conforma-

extensively reported in the literature [13,14]. Azo ligands are most important objects of the modern coordination chemistry [15–18].

The preparation of new ligands is perhaps the most important step

in the development of metal complexes with unique properties and

novel reactivity [19]. The second order NLO organic materials are

typically based on NLO chromophores that can be incorporated in

polymer [20-24] or hybrid organic-inorganic [24,25] or in cross

linked system [26]. The dendritic approach, in which the chromo-

phore is functionalized with branched bulky groups to hinder its

tendency to crystallize has also been largely employed in the recent

years [27,28]. In all these approaches the choice of the proper

chromophore plays a fundamental role: high NLO activity,

tions of some arylazosalicylaldehyde and their oximes by theoretical methods and spectral studies [29]. These aldehydes can be used as starting materials to synthesize of some dialdehydes, which in







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Iable I				
Physical and	mass	spectral	values	of 1–3 .

Compds.	Physical		Mass (<i>m</i> / <i>z</i>)	
	Colour	Yield (%)	m.p. (°C)	
1	Yellowish orange	66	194-195	478.0 [M], 448.1 [M-1], 418.3 [M-2]
2	Yellowish orange	52	220-221	506.0 [M], 475.3 [M-2], 446.7 [M-1]
3	Yellow	40	240-241	554.1 [M], 524.2 [M-1], 494.3 [M-2], 331.2 [M+1]

turn can be used as colourimetric receptor for some ions. Further these dialdehydes can be used to synthesize several coordination complexes, fused macrocycles, oxazolidines, pyrimidines and so on. In continuation of this work, some 1,n-di(2-formyl-4phenylazophenoxy)alkanes 1-3 were synthesized and characterized in the present study, and their conformations have been predicted from theoretical studies. Selected geometrical properties, NBO, AIM analysis, HOMO-LUMO, MEP surface, dipole moment, polarizability and first order hyperpolarizability were determined by the density functional theory (DFT) method and analysed.

Table 2

Table 1

IR spectral values (cm^{-1}) of **1–3**.

Assignments	1	2	3
Varomatic(C–H)	3063	3041	3063
$v_c = 0$	1686	1683	1687
$v_{c}=_{c}$	1569	1593	1594
	1480	1485	1483
v _N =_N	1248	1253	1255
v_{C-O}	1092	1090	1092
Aromatic CH out-of-plane bending vibration	817	824	822
	764	770	770
	686	686	689

2. Experimental

2.1. Synthesis of 5-arylazosalicylaldehyde

5-Arylazosalicylaldehyde was prepared following the procedure mentioned in the literature [30]. A mixture of aniline (≈ 0.93 g, 1 mmol), water (15 mL) and 5 N HCl (10 mL) was cooled to 0–5 °C and to this a solution of sodium nitrite (0.69 g, 1 mmol) in water was added. The mixture was stirred for 30 min in an ice bath. Diazonium salt was obtained and this was added in drop wise to an ice-cold solution of salicylaldehyde (1 mL, 1 mmol) and 10% sodium hydroxide (10 mL) for 1 h with constant stirring. The solid mass separated out was removed by filtration, dried and recrystallized from ethanol.

2.2. Synthesis of 1,n-di(2-formyl-4-phenylazophenoxy)alkanes **1** and **2** and 1,3-di(2-formyl-4-phenylazophenoxymethyl)benzene **3**

A mixture of 5-arylazosalicylaldehyde (0.46 g, 2 mmol), alkyldibromides (1 mmol) [1,2-dibromoethane (0.12 mL), 1,4dibromobutane (0.11 mL) and *m*-dibromoxylene (0.26 g)] and potassium carbonate (0.5 g) in acetonitrile (15 mL) was refluxed for 24 h. The reaction mixture was filtered and the solvent was evaporated to obtain 1,*n*-di(2-formyl-4-phenylazophenoxy)alkanes **1** and **2** and 1,3-di(2-formyl-4-phenylazophenoxymethyl)benzene **3**.



Fig. 1. IR spectrum of 1.



Scheme 1. Steps involved in the synthesis of 1–3.

The pure product was obtained by recrystallization from ethanol. The physical and mass spectral data of all the synthesized compounds **1–3** are displayed in Table 1. The mass spectrum of **2** is given in Fig. S1.

Avatar-330 FT-IR spectrophotometer was used for recording IR spectra (KBr pellet). The mass spectra were performed using JEOL Gcmate spectrometer. The UV–visible spectra were recorded in Shimadzu UV-1800 UV–visiblespectrophotometer using N,N-dimethylformamide as solvent at ambient room temperature.

2.3. Spectral measurements

The ¹H (500 MHz) and ¹³C NMR (125 MHz) were recorded at room temperature on Bruker 500 MHz instrument using 10 mm sample tube. Samples were prepared by dissolving about 10 mg of the sample in 2.5 mL of chloroform-*d* containing 1% TMS for ¹H and 50 mg of the sample in 2.5 mL of chloroform-*d* containing a few drops of TMS for ¹³C. The solvent chloroform-*d* also provided the internal field frequency lock signal. The ¹H–¹H and ¹H–¹³C COSY spectra were performed on a Bruker 500 NMR spectrometer.

2.4. Computational study

Geometry optimizations were carried out according to density functional theory available in Gaussian-03 package using B3LYP/6-31G(d,p) basis set [31] available in Gaussian-03 package. The polarizabilities and hyperpolarizabilities were determined from the DFT optimized structure by finite field approach using B3LYP/6-31G* basis set, NBO calculations using the basis set B3LYP/6-311+G(d,p) available in Gaussian-03 and AIM calculations were





Fig. 3. ¹³C NMR spectrum of 1.

done using B3LYP/6-31G(d,p) basis set.

3. Results and discussion

3.1. FT-IR spectra

The sharp peaks around 1680 cm⁻¹ in the FT-IR spectra of **1–3** are due to $v_{C}=_0$ of aldehydic group. Strong peaks for -N=N-(azo) group are observed in the region 1250 cm⁻¹. The aromatic and aliphatic C–H stretching vibration appeared around 3060 and 2870 cm⁻¹, respectively. The peaks around 1090 cm⁻¹ are attributed to aliphatic v_{C-0} mode. The FT-IR spectral data of **1–3** are listed in Table 2 and FT-IR spectrum of **1** as shown in Fig. 1.

3.2. NMR spectra

1,*n*-di(2-Formyl-4-phenylazophenoxy)alkanes **1** and **2** and 1,3di(2-formyl-4-phenylazophenoxymethyl)benzene **3** were



Fig. 4. Possible conformations of 1-3.

Table 3

¹H Chemical shifts (ppm) of **1–3**.

Compds.	H-3	H-5	H-6	H-10 and H-14	H-11 and H-13	H-12	H-16	H-18 and H-18'	H-19 and H-19'	H-20	H-21 and H-22
1	8.46 (d, 2.50)	8.20 (dd, 2.50, 8.50)	7.22 (d, 8.50)	7.92 (d, 7.50)	7.52 (t)	7.49 (t)	10.53 (s)	4.67 (s)	-	-	-
2	8.46 (d, 2.50)	8.19 (dd, 2.75, 8.75)	7.17 (d, 8.50)	7.93 (d, 7.00)	7.54 (t)	7.50 (t)	10.58 (s)	4.34 (t)	2.21 (t)	_	
3	8.48 (d, 2.50)	8.18 (dd, 2.75, 8.75)	7.21(d, 9.00)	7.93 (d, 8.25)	7.49–7.55	7.49–7.55	10.63 (s)	5.36 (s)	-	7.60	7.49–7.55

Values within parentheses are the observed coupling constants in Hz.

Table 4	
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¹³C Chemical shifts (ppm) of **1–3**.

Compds.	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(9)	C(10) and C(14)	C(11) and C(13)	C(12)	C(16)	C(18)	C(19)	C(20)	C(21)	C(22)
1	162.03	125.47	123.93	147.02	129.84	113.02	152.42	122.88	129.13	131.14	188.71	67.26	_	_	_	_
2	162.68	125.11	123.89	146.54	129.97	112.81	152.46	122.83	129.12	131.01	189.05	68.46	25.91	_	_	_
3	162.34	125.44	123.91	146.76	129.82	113.41	152.44	122.85	129.13	131.07	189.14	70.66	136.39	126.13	127.43	129.46

synthesized as shown in Scheme 1 and characterized by ¹H, ¹³C NMR, ¹H–¹H and ¹H–¹³C COSY spectra. The labelling of the atoms followed in the present study was indicated in Scheme 1. The signals in the ¹H NMR spectrum were assigned based on their positions, integrals and multiplicities. The 500 MHz NMR spectrum of **1** (Fig. 2) reveals a sharp singlet at 4.67 ppm for the methylene protons attached to oxygen atom O(15) *i.e.*, H(18) and H(18'). The low frequency doublet centered at 7.22 ppm is assigned to the *ortho* proton with respect to OCH₂ moiety *i.e.*, H(6). The doublet centered at 8.46 ppm (integral corresponds to two protons) and doublet of doublet centered at 8.20 ppm (integral corresponds to two protons) are assigned to the ring protons H(3) and H(5), respectively [32].

The doublet nature of the signal for H(3) (J = 2.50 Hz) is due to *meta* coupling with respect to OCH₂ moiety and another coupling is also observed in the signal of H(5) (J = 2.50, 8.50 Hz), which appeared as doublet of doublet due to $4J_{3,5}$ coupling of H(5). The NMR spectrum further reveals high frequency doublet at 7.92 ppm for the *ortho* protons of the phenyl ring attached to the nitrogen atom N(8) *i.e.*, H(10) and H(14). Two triplets at 7.52 (integral corresponds to four protons) and 7.49 ppm (integral corresponds to two protons) are also observed for *meta* [H(11) and H(13)] and *para* [H(12)] protons, respectively of the phenyl ring attached to nitrogen atom N(8). The high frequency singlet at 10.53 ppm is assigned to aldehydic proton H(16). This assignment is further confirmed by the correlation



Fig. 5. Optimized structures of 1-3.

observed in the ${}^{1}H-{}^{1}H$ COSY spectrum (Fig. S2). In a similar manner assignments were done for other compounds **2** and **3**.

In ¹³C NMR spectra at 125 MHz have been recorded in CDCl₃ for 1–3. The assignment of signals in 1 is made as follows (Fig. 3). The low frequency signal at 67.26 ppm is due to the methylene carbon attached to oxygen atom O(15) *i.e.*, C(18). The high frequency signal at 188.71 ppm is due to aldehvdic carbon C(16). The signal at 113.02 ppm is due to *ortho* carbon with respect to oxygen atom O(15) *i.e.*, C(6). The high intense signals at 122.88 and 129.13 ppm are due to ortho [C(10) and C(14)] and meta [C(11) and C(13)] carbons of the phenyl ring attached to nitrogen atom N(8). The ¹³C NMR spectrum reveals four signals for quaternary carbons C(1), C(2), C(4) and C(9) at 162.03, 125.47, 147.02 and 152.42 ppm, which can easily be distinguished from other carbons based on small intensities. Among the signals for quaternary carbons, the high frequency signal at 162.03 ppm is assigned to the *ipso* carbon C(1) and this assignment is based on the high deshielding nature of the oxygen atom compared to nitrogen and carbon atoms. The signal at 125.47 ppm is assigned to the ipso carbon C(2), since it is ortho with respect to oxygen atom O(15). Among the remaining signals at 152.42 and 147.02 ppm, the signal at 147.02 ppm is assigned to the carbon C(4) which is para with respect to the OCH₂ moiety. Obviously, the signal at 152.42 ppm is assigned to the *ipso* carbon C(9)

Table 5

Selected geometric parameters [bond lengths (Å), bond angles (°) and torsional angles (°)] of 1–3.

Geometric parameters	1	2	3
Bond length			
C1-C2	1.41	1.42	1.42
C2-C3	1.40	1.40	1.40
C2-C16	1.48	1.48	1.48
C1-C6	1.41	1.41	1.41
C1-015	1.36	1.36	1.38
C4-N7	1.42	1.42	1.42
O15-C18	1.42	1.43	1.47
N7-N8	1.26	1.26	1.28
C16-017	1.22	1.22	1.25
C16–H16	1.11	1.05	1.10
N8-C9	1.42	1.42	1.42
C18–C18′	1.52	-	-
C18–C19	-	1.52	1.51
C19–C19′	-	1.53	-
Bond angle			
C1–C2–C3	119.0	119.1	118.9
C1-C2-C16	121.9	121.7	121.4
C2-C1-C6	120.0	119.7	120.3
C2-C1-O15	116.5	116.5	116.2
C6-C1-O15	123.5	123.7	123.6
C1-015-C18	119.5	119.7	119.9
C2-C16-017	123.4	123.4	123.3
C2-C16-H16	115.7	115.7	116.3
017–C16–H16	120.9	120.9	120.5
015–C18–C19/015–C18–C18′	105.9	107.3	108.0
C18–C19–C19′	-	112.0	-
Torsional angle			
C3-C2-C1-015	-180.0	180.0	-179.6
C16–C2–C1–C6	-180.0	180.0	-179.6
C1–C2–C16–O17	-180.0	180.0	-178.7
C1-C2-C16-H16	0.0	-0.0	1.4
C3-C2-C16-017	0.0	0.0	1.3
C3-C2-C16-H16	-180.0	-180.0	-178.6
015-C1-C6-C5	180.0	-180.0	179.7
C6–C1–O15–C18	-0.0	0.1	-1.8
C3-C4-N7-N8	-180.0	179.9	179.9
C1-015-C18-C19	-180.0	179.8	-179.0
N7–N8–C9–C10	0.0	-0.1	-0.2
015-018-019-020	_	-	47.0
015 - C18 - C19 - C21	_	-	-134.7
	-	180.0	-
015-018-018'-015'	-180.0	-	-

which is attached to the nitrogen atom N(8). The remaining signals at 131.14, 129.84 and 123.93 ppm are assigned to the carbons C(12), C(5) and C(3), respectively. This assignment is based on correlations observed in the ^{1}H — ^{13}C COSY spectrum (Fig. S3). In a similar manner assignments were done for other compounds **2** and **3**. The ^{1}H and ^{13}C chemical shifts obtained in this manner are listed in Tables 3 and 4, respectively.

3.3. UV-vis absorption spectra

UV–Vis absorption spectra are recorded for **1–3** in dimethylformamide in the region 260–400 nm. The maximum absorption bands exhibit of 328.5, 335.0 and 339.5 nm for the dialdehydes **1–3**, respectively. All the absorption bands are due to the π – π * transition of the –N=N– unit. The higher λ_{max} is observed for **3**, when compared to other **1** and **2** due to the presence of *m*-xylene moiety linked between two arylazosalicylaldehyde moiety. The UV–Vis absorption spectra of **1–3** are shown in Fig. S4.

3.4. Conformational analysis

The presence of only one set of signals for phenylazosalicylaldehyde moiety and methylene moiety indicates that the dialdehydes are symmetric molecules. Therefore there are two possible conformations for 1–3. In conformation **A** the two aldehydic moieties (CH=O groups) are opposite to each other whereas in conformation **B** the two aldehydic moieties are [CH=O group] on the same side (Fig. 4). The possibility of existing in conformation **B** is ruled out since severe steric crowding exists between the two aldehydic moieties. Therefore, the dialdehydes exist in conformation **A** only. In order to confirm this, geometry optimizations were done for both the possibilities for **1**. The energies are found to be –1600.0535 and –1600.0429 Hartree for conformations **A** and **B**,

Table 6 HOMO-LUMO energies (eV) and dipole moment $\mu(D)$ of **1–3**.

Compds.	НОМО	LUMO	ΔΕ	Dipole moment
1	-6.196	-2.399	3.797	1.01
2	-6.123	-2.318	3.085	1.09
3	-6.096	-2.469	3.627	7.08

Table 7Polarizabilities and hyperpolarizabilities for 1–3.

	1	2	3
α _{xx}	776.458	798.067	782.773
α_{xy}	-78.092	93.064	-37.324
ayy	370.784	397.808	435.432
$\alpha_{\rm xz}$	-0.011	-0.008	46.610
α _{yz}	0.002	0.011	14.290
a.zz	118.487	135.876	252.026
<a> (a.u)	421.910	443.917	490.077
$10^{24} \times \alpha_{tot}$	62.527	65.788	72.629
β_{xxx}	-3.823	2.820	-173.595
β _{xxy}	-2.038	-9.781	-1979.258
β _{xyy}	7.961	14.060	194.219
β _{yyy}	-0.345	-18.074	-199.901
β_{xxz}	4.596	-15.182	50.035
β _{xyz}	2.581	-7.451	-67.127
β _{yyz}	-1.546	2.525	125.441
β _{xzz}	-1.775	-0.985	23.573
β _{yzz}	2.231	-2.455	125.497
β _{zzz}	-4.902	-0.879	171.366
β _{tot} (a.u)	9.034	36.805	1690.415
$10^{33} \times \beta_{tot} (esu)$	78.044	317.967	14604.005

respectively. From the values the favoured conformation is predicted to be A for 1. The other dialdehydes also exist in conformation A only. The optimized structures of favoured conformations are displayed in Fig. 5.

3.5. Molecular properties

3.5.1. Geometric parameters

From the optimized structures of geometric parameters were derived in Table 5. The observed torsional angles O(15)-C(18)-C(19)-C(20) [47.0°] and O(15)-C(18)-C(19)-C(21) [-134.7°] in dialdehyde **3** indicate that the phenyl ring of xylene moiety is highly distorted from the plane containing 4phenylazobenzaldehydic moiety. In dialdehydes 1 and 2, the torsional angles O(15)-C18-C(18')-O(15') and O(15)-C(18)-

HOMO

C(19)-C(19') are found to be -180.0° and 180.0° , respectively.

3.6. Energies, dipole moments and polarizabilities

HOMO-LUMO energies, dipole moments, polarizability and first order hyperpolarizability for the dialdehydes **1–3** were calculated and the values are listed in Tables 6 and 7. HOMO-LUMO pictures are reproduced in Fig. 6. From Table 6 it is seen that the energies of both HOMO and LUMO orbitals are increased as the number of carbon atoms in the side chain increased but the energy gap decreased. The order of dipole moments are 3 > 2 > 1.

HOMO orbitals are mainly derived from *pz* orbitals of carbon nitrogen and oxygen atoms except *pz* orbitals of aldehydic carbon C(16), *pz* orbital of alkoxy carbons $(CH_2)_n$ in dialdehydes **1** and **2**. In 3, the *pz* orbitals of one of the 2-formyl-4-phenylazo-



3

Fig. 6. HOMO-LUMO pictures of 1-3.

phenoxymethyl moiety and *pz* orbitals of central benzene ring are not taking part in the formation HOMO orbitals. LUMO orbitals are derived from *pz* orbitals of carbon, nitrogen and oxygen atoms except *pz* orbitals of C(6), C(11), C(13) and *pz* orbital of alkoxy carbons in **1** and **2**. In **3** the *pz* orbitals of one of the 2-formyl-4phenylazophenoxymethyl moiety, *pz* orbitals of central benzene ring and *pz* orbitals of C(6), C(11) and C(13) are not taking part in the formation LUMO orbitals.

The polarizabilities and first-order polarizabilities were also calculated by DFT method using the basis set B3LYP/6-31G* available in Gaussian-03 package and these values are listed in Table 7. Increase in the number of carbon atoms in the side chain increased both the polarizabilities and hyperpolarizabilities. The NLO character decreases according to the following order: 3 > 2 > 1.

3.7. NBO analysis

NBO analysis at B3LYP/6-311+G(d,p) level were carried out for the dialdehydes **1–3** and the important second-order perturbative estimates of donor–acceptor interactions are displayed in Table S1. The π -bonded electrons of C(2)–C(3) and C(6)–C(5) bonds in **1–3** are delocalized on to the non-bonding *p*-orbitals available on C(4) carbon atom, which in turn delocalized on to the nearby antibonding orbitals of the *vicinal* C(2)–C(3), N(7)–N(8) and C(6)–C(5) bonds. The hyperconjugative interaction energies involving C(4) *p*-



Fig. 7. MEP diagrams of 1-3.

orbital with the antibonding orbitals of vicinal C(2)–C(3), N(7)–N(8) and C(6)–C(5) bonds are found to be very high (\approx 78, 63, 74 kcal mol⁻¹) and this is the primary delocalization in dialdehydes **1–3**.

3.8. AIM analysis

Atoms in molecules electron density topological analysis carried out for aldehyde 1 revealed the existence of 56 bond critical points (BCPs) with a (3, -1) topology between the atoms connected by covalent bond (Table S2). The negative values obtained for the Laplacian are clear indication that the electronic charge is locally concentrated within the region of inter atoms leading to an interaction named as covalent bonds and being characterized by large $\rho_{\rm b}$ values. Besides these one more bond critical point is observed between the atoms C(16) and O(17) (aldehyde carbonyl group). The value of ρ_{BCP} at the BCP is found to be 0.402 and $\nabla^2 \rho_{BCP}$ value is found to be 0.279 (C16–O17). The positive magnitude of $\nabla^2 \rho_{BCP}$ indicates the highly ionic nature of carbonyl group in aldehyde 1. In other aldehydes 2 and 2 also ionic nature of carbonyl (C16–O17) group (Table S2) is confirmed by the positive Laplacian density at bond critical point and high ρ_{BCP} values. Ring critical point (RCP) of phenyl ring attached to N(8) [(C9-C10-C11-C12-C13-C14)] is slightly having higher electron density compared to the phenyl ring of the benzaldehyde moiety [C1-C2-C3-C4-C5-C6].

3.9. MEP surfaces

Three-dimensional distribution of molecular electrostatic potential (MEP) is highly useful in predicting the reactive behaviour of the molecule. The MEP surface has been plotted for aldehydes and representative diagram is given in Fig. 7. Region of negative charge (red colour (in the web version)) is seen around the electronegative oxygen O(17) and O(17') in dialdehydes **1–3**. The red colour region is susceptible for electrophilic attack. Blue colour represents strongly positive region and the predominant green region in the MEP surfaces corresponds to a potential half way between the two extreme [red and blue] regions in aldehydes **1–3**.

4. Conclusions

Structure of 1,*n*-di(2-formyl-4-phenylazophenoxy)alkanes **1** and **2** and 1,3-di(2-formyl-4-phenylazophenoxymethyl)benzene **3** were analysed by 1D, 2D NMR and mass spectral studies. The stable conformation of **1**–**3** were predicted theoretically and molecular parameters of HOMO-LUMO energies, polarizabilities, hyperpolarizabilities, NBO and AIM analysis were calculated using Gaussian-03 package.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.molstruc.2015.10.006.

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