Journal of Physical and Theoretical Chemistry
of Islamic Azad University of Iran, 11 (2) 93-102: Summer 2014
(J. Phys. Theor. Chem. IAU Iran)
ISSN 1735-2126

Molecular structure, substitution effect, solvent effect and properties of niobapyrimidinium complex: A computational study

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Received July 2014; Accepted August 2014

ABSTRACT

The structure and properties of niobapyrimidinium complex were examined by density functional theory method (mpw1pw91). The effect of solvent on the structural parameters, frontier orbital energies and hyperpolarizability (β_{tot}) of this molecule has been explored. The thermodynamic properties of the title compound at different temperatures have been calculated. Also, the *para*-substitutions effect on the structure, frontier orbital energies, aromaticity and hyperpolarizability (β_{tot}) has been studied. Nucleus independent chemical shift (NICS) values show that these species are aromatic.

Keywords: Niobapyrimidinium Complex; Solvent Effect; Substitution Effect; Hyperpolarizability; Aromaticity

INTRODUCTION

Metallabenzenes are organic/transition-metal "hybrids" which possess aromatic properties. They have been revealed numerous similarities to heterobenzenes: downfield chemical shifts for ring protons, planarity of the six membered metallacycle, no alternation of bond lengths, and even electrophilic aromatic substitution [1-11]. There is now an extensive amount of relevant synthetic, structural, spectral, computational, and reactivity data for metallabenzenes. Also, the structure and properties of metallabenzenes have been studied theoretically [9,12-18]. Also, metallapyrimidines fall into the general group of metallaaromatics. For example, metallapyrimidines and metallapyrimidiniums synthesized from oxidative addition of pyrazolate N−N Bonds to Niobium(III), Niobium(IV), and Tantalum(IV) Metal Centers [19].

In the present study, the geometries and properties of niobapyrimidinium are investigated theoretically. The *para*-substitution and solvent effect on the structure, frontier molecular orbital energies, hyperpolarizability have been explored. Also, standard thermodynamic functions of the

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niobapyrimidinium compound have been calculated in various temperatures.

COMPUTATIONAL METHODS

All calculations were carried out with the Gaussian 03 suite of program [20]. The calculations of systems contain C, Br, O, N, Cl, F and H described by the standard 6-311G(d,p) basis set [21-24]. For niobium element standard LANL2DZ basis set [25-27] are used and niobium described by effective core potential (ECP) of Wadt and Hay pseudopotential [25] with a doublet-ξ valance using the LANL2DZ. Geometry optimization was performed utilizing with Modified Perdew-Wang Exchange and Correlation (mpw1pw91) [28]. The results of calculations for transition metal complexes show that MPW1PW91 functional gives better results than B3LYP [29-32]. A vibrational analysis was performed at each stationary point found, that confirm its identity as an energy minimum.

For the solvation effects study we have used a self-consistent reaction field (SCRF) approach, in particular using the polarizable continuum model (PCM) [33].

Geometries were optimized at this level of theory without any symmetry constraints followed by the calculations of the first order hyperpolarizabilities. The total static first hyperpolarizability β was obtained from the relation:

$$\beta_{tot} = \sqrt{\beta_x^2 + \beta_y^2 + \beta_z^2} \tag{1}$$

upon calculating the individual static components

$$\beta_i = \beta_{iii} + \frac{1}{3}\sum_{i \neq j} (\beta_{ijj} + \beta_{jij} + \beta_{jji}) \tag{2}$$

Due to the Kleinman symmetry [34]:

$$\beta_{xyy} = \beta_{yxy} = \beta_{yyx} ; \beta_{yyz} = \beta_{yzy} = \beta_{zyy}, \ldots \tag{3}$$

one finally obtains the equation that has been employed:

$$\beta_{tot} = \sqrt{(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2} + \sqrt{(\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2} + \sqrt{(\beta_{zzz}\, zxx + \beta_{zyy})^2} \tag{4}$$

The nucleus-independent chemical shift (NICS) index, based on the magnetic criterion of aromaticity, is probably the most widely used probe for examination of chemical compounds aromatic properties [35]. It is defined as the negative value of the absolute magnetic shielding. NICS values are calculated using the Gauge independent atomic orbital (GIAO) [36] method at the B3LYP/6-311G(d,p) level of theory.

GaussSum 2.2.6.1 was used to prepare total density of state (TDOS) or density of state [37].

RESULT AND DISCUSSION

Energy

The molecular structure and atomic numbering of niobapyrimidinium complexes is presented in Figure 1. The energies of *para*-substituted niobapyrimidinium complexes in gas phase and niobapyrimidinium complex in different media by using the PCM model are collected in Table. E_T is the total energy and ΔE_{solv} is the stabilization energy by solvents, the relative energy of the title compound in a solvent to that in the gas phase.

From Table 1, we can see that the calculated energy is dependent on the magnitude of the dielectric constant of solvents. In the PCM model, the absolute energies decrease with the increasing dielectric constants of solvents. On the other hand, ΔE_{solv} values indicate to increasing of stability in more polar solvents. This is because a dipole in the molecule will induce a dipole in the medium, and the electric field applied to the solute by the solvent (reaction) dipole will in turn interact with the molecular dipole to lead to net stabilization. This implies that the niobapyrimidinium complex has more stability in polar solvent rather than in the gas phase.

Table 1. Dielectric constant of solvent, absolute energy (E, Hartree), solvent stabilization energies (E_{solv}), and), dipole moment (μ, Debye), values niobapyrimidinium complex in different media by using the PCM model

	ε	E	E_{solv}	μ
gas	-	-508.2573	-	9.18
Di Chloro Ethane	10.36	-508.2933	-22.58	17.50
Quinoline	9.03	-508.2924	-22.02	17.07
Di Chloro Methane	8.93	-508.2921	-21.88	17.06
THF	7.58	-508.2903	-20.75	16.59
Aniline	6.89	-508.2896	-20.26	16.33
Di Ethyl Ether	4.335	-508.2832	-16.29	14.90

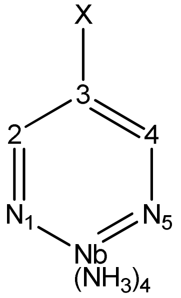

Fig. 1. The molecular structure and atomic numbering of *para*-substituted niobapyrimidinium complexes.

Dipole moment

Dipole moment values of *para*-substituted niobapyrimidinium complexes in gas phase and niobapyrimidinium complex in different media by using the PCM model are collected in Table 1. These values illustrate the solvent effect on the stabilization energy is in parallel with that on the dipole moment of the solute. A good linear relationship between the solvent stabilization energies and the dipole moments of niobapyrimidinium complex in the set of solvents is shown in Figure 2, that is to say, there is the larger the dipole moment of solute, and the higher the stabilization energy in the stronger the solvent polarity.

Molecular orbital analysis

The energies of the frontier orbitals (HOMO, LUMO) along with the corresponding HOMO–LUMO energy gaps, Hardness, chemical potential, and electrophilicity for *para*-substituted niobapyrimidinium complexes in gas phase niobapyrimidinium complexes and in different media by using the PCM model are given in Tables 2 and 3.

As seen from Table 3, inclusion of solvation effects leads also to changes on the molecular orbital energies. In solution, HOMO is stabilized, with respect to the corresponding values in vacuum. There is a linear correlation between HOMO energy and dielectric constant (R^2=0.938). On the other hand, the energies of LUMO in solvated media are higher than the corresponding values computed in vacuum. On the other hand, HOMO-LUMO, electrophilicity and chemical potential values are decrease in solution phase. There are linear correlations between these values and dielectric constant (R^2=0.905: HOMO-LUMO, 0.976: μ, 0.904: ω).

The replacement of *para*-hydrogen atom of niobapyrimidinium by different groups has the effect to frontier orbital energies. In the presence of electron withdrawing substituents (X=CN, CHO, NO_2), HOMO and LUMO energies is lower than donor electron substituents. Also, hardness, chemical potential and ω (electrophilicity index) of donor electron groups are less than withdrawing electron.

Table 2. Frontier orbital energies (Hartree), HOMO-LUMP gap (ΔE, eV), hardness (ηeV), chemical potential (μ,eV), and electrophilicity (ω,eV), values of *para*-substituted niobapyrimidinium in gas phase

structure	HOMO	LUMO	ΔE	η	μ	ω
H	-0.087	-0.003	2.30	1.15	-1.23	0.66
F	-0.096	-0.008	2.41	1.20	-1.41	0.82
Cl	-0.101	-0.011	2.46	1.23	-1.53	0.96
Br	-0.102	-0.012	2.46	1.23	-1.55	0.98
Me	-0.088	-0.004	2.28	1.14	-1.24	0.68
NH_2	-0.085	-0.002	2.25	1.13	-1.19	0.63
OH	-0.089	-0.004	2.33	1.16	-1.27	0.69
OMe	-0.092	-0.006	2.33	1.17	-1.34	0.77
CN	-0.113	-0.019	2.55	1.27	-1.79	1.26
CHO	-0.107	-0.016	2.46	1.23	-1.68	1.14
NO_2	-0.115	-0.027	2.40	1.20	-1.94	1.56

Table 3. Frontier orbital energies (Hartree), HOMO-LUMO gap (ΔE, eV) of niobapyrimidinium complex in different media by using the PCM model

	HOMO	LUMO	ΔE	η	μ	ω
gas	-0.087	-0.003	2.295	1.148	-1.230	0.659
DiChloroEthane	-0.101	0.004	2.848	1.424	-1.326	0.617
Quinoline	-0.101	0.004	2.843	1.422	-1.320	0.613
DiChloroMethane	-0.101	0.004	2.839	1.419	-1.317	0.611
THF	-0.100	0.004	2.808	1.404	-1.308	0.609
Aniline	-0.099	0.004	2.803	1.401	-1.303	0.606
DiEthylEther	-0.096	0.003	2.694	1.347	-1.276	0.604

Table 4. Selected structural parameters (in Å), niobapyrimidinium complex in different media by using the PCM model

		NbN	NC	CC
gas		1.885	1.341	1.402
DiChloroEthane	10.36	1.885	1.349	1.404
Quinoline	9.03	1.886	1.348	1.404
DiChloroMethane	8.93	1.885	1.349	1.404
THF	7.58	1.885	1.348	1.404
Aniline	6.89	1.885	1.348	1.404
DiEthylEther	4.335	1.885	1.347	1.403

Bond distances

It is well-known that the solvent polarity influences both the structure and properties of conjugated organic molecules and metal complexes [38-40]. The structural data for the optimized structures of niobapyrimidinium complex in the five studied solvents are collected in Table 5. The results show that the structural parameters are changed by the polarity of the surrounding media. These values indicate lengthening of C-C and C-N bonds in the set of solvents rather than gas phase. Also, these values show that d(CN) and d(CC)increases with increasing of dielectric constant of solvent. On the other hand, d(NbN) are almost constant in different solvents.

The selected bond distances of *para*-substituted niobapyrimidinium complexes have been listed in Table 4. The Nb-N bond lengths show that lengthening of these bonds in withdrawing electron groups (X=CN, NO$_2$, CHO). In the literature, we have found experimental data for (2,2,6,6-tetramethyl-5-ketimidohept-3-en-3-imide)bis(3,5-di-tert-butylpyrazolate)niobium(V) and compared these values with our calculations. In synthesized complex Nb-N1, N1-C1, C1-C2 bonds are different with Nb-N5, N5-C4, C4-C3, respectively. The average of bond lengths of any bond is similar to our calculated values.

Density of states (DOS)

To realize the fundamental features of bonding interactions of niobapyrimidinium complex, we performed density of states of the total (TDOS), partial (PDOS), and crystal orbital overlap population (COOP). The DOS, PDOS, and COOP niobapyrimidinium complex are sketched in Figure 3.

The PDOS essentially indicates the composition of the fragment orbitals contributing to the molecular orbitals. As clearly shown in this figure, the PDOS reveals that the HOMO and LUMO are fairly localized on NH$_3$ and with fewer contributions from other fragments.

The OPDOS illustrates the nonbonding, bonding and antibonding nature of the interaction of the two atoms, orbitals or groups. Zero value of the OPDOS indicates nonbonding interactions. The positive and negative values indicate the bonding and anti-bonding interaction. In addition, the OPDOS diagrams permit us to the resolve and comparison of the donor–acceptor features of the ligand and determine the bonding, non-bonding.

Nucleus independent chemical shift (NICS)

Table 6 encloses the values corresponding to NICS aromaticity criteria [35]. NICS values have been calculated in center and 0.5, 1.0, 1.5, and 2.0 Å above of the center of rings. In all substituents (except X=NO$_2$), the most negative NICS values are 0.5 Å above of the rings center. This value is 1.0 Å above of the center of ring in X=NO$_2$. This is compatible with π-aromaticity in these rings. Also, the NICS values exhibit increasing of aromaticity in electron withdrawing substituents.

Table 5. Selected structural parameters (in Å) *para*-substituted niobapyrimidinium in gas phase

	NbN	NC	CC
exp	1.841	1.306	1.428
	1.927	1.373	1.354
	1.884	1.3395	1.391
H	1.88517	1.34055	1.40192
F	1.88520	1.34098	1.39462
Cl	1.88581	1.33764	1.39995
Br	1.88599	1.33772	1.40081
Me	1.88372	1.33969	1.40537
NH$_2$	1.88199	1.34025	1.40645
OH	1.87729	1.34157	1.39967
OMe	1.88598	1.33953	1.40119
CN	1.88870	1.32946	1.41563
CHO	1.89844	1.32780	1.41398
NO$_2$	1.89339	1.32717	1.41045

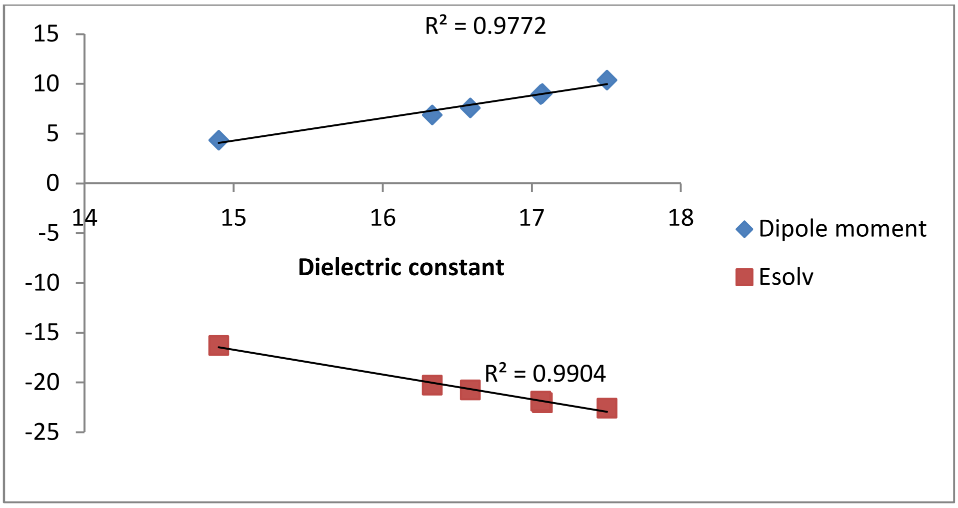

Fig. 2. Linear relationship of dielectric constants values with dipole moment and salvation energies in niobapyrimidinium complex.

Table 6. NICS values for *para*-substituted niobapyrimidinium

	NICS(0.0)	NICS(0.5)	NICS(1.0)	NICS(1.5)	NICS(2.0)
H	-9.2814	-10.1140	-9.7147	-7.4579	-5.2062
F	-9.2816	-9.5505	-8.6522	-6.4744	-4.4204
Cl	-8.7462	-9.8882	-9.7892	-7.5825	-5.3768
Br	-8.7108	-9.8212	-9.7158	-7.5239	-5.3077
Me	-9.1831	-9.7238	-9.3315	-7.1557	-4.9321
NH_2	-8.5636	-9.6968	-9.2749	-7.5581	-6.6662
OH	-8.4691	-8.9284	-8.3545	-6.4190	-4.5416
OMe	- 8.2539	- 9.3218	- 8.8821	- 6.8504	- 5.0940
CN	- 10.7005	- 11.6888	- 11.1444	- 8.3829	- 5.7109
CHO	-10.1861	-11.7073	-11.5228	-8.6767	-5.9324
NO_2	-9.7800	-11.8410	-12.0035	-8.9761	-6.1270

Table 7. Standard thermodynamic functions of the niobapyrimidinium compound

T	G	H	S	C_v
100	-508.056945	-508.043728	82.941	29.056
200	-508.072401	-508.037373	109.900	46.062
300	-508.091722	-508.028624	131.982	59.229
400	-508.114309	-508.017999	151.089	69.785
500	-508.139764	-508.005850	168.065	78.427
600	-508.167787	-507.992450	183.375	85.543
700	-508.198138	-507.978013	197.329	91.518
800	-508.230620	-507.962692	210.159	96.662
900	-508.265069	-507.946604	222.044	101.176
1000	-508.301347	-507.929839	233.125	105.182

Thermodynamic parameters

On the basis of statistical thermodynamic principle, heat capacities (C_v ,m in cal K^{-1} mol^{-1}), entropies (S, in cal K^{-1} mol^{-1}), and enthalpies (H, in kcal mol^{-1}) at ranging from 100 to 10000 K were obtained and gathered in Table 7. As can be seen from Table 7, the C_v, S, and H thermodynamic functions of niobapyrimidinium all increase as the temperature increases. This is for the reason that the vibrational movement is invigorated at the higher temperature and makes more contributions to the thermodynamic functions, although at the lower temperature, the main contributions are due to the translation and rotation of the molecules. The relationships between the thermodynamic functions and the temperature in 100–1000 K for, are expressed as:

$H = 6\text{-}.18 \times 10^{-7} T^2 – 6.10 \times 10^{-5} T - 508.05; R^2 = 0.99253$

$C_V = -7.41 \times 10^{-5} T^2 – 1.62 \times 10^{-1} T +15.60; R^2 = -0.995151$

$S = -8.82 \times 10^{-5} T^2 + 2.59 \times 10^{-1} T +60.21; R^2 = 0.99029$

$G = -1.268 \times 10^{-7} T^2 - 1.35 \times 10^{-4} T - 508.04; R^2 = -0.99317$

Hyperpolarizability

Theoretical investigation assists a fundamental role in comprehending the structure-property correlation, which is able to maintain in designing novel NLO chormophores. The electrostatic first hyperpolarizability (β_{tot}) and dipole moment (μ) of the *para*-substituted niobapyrimidinium complexes in gas phase niobapyrimidinium complex and niobapyrimidinium in different media have been calculated. As seen from Table 8, it is found that largest β_{tot} values is $X=NH_2$ complex, which is attributed to the positive contribution of their conjugation. On the other hand, solvent effect on hyperpolarizability values show increasing of β_{tot} values by decreasing of dielectric constants for niobapyrimidinium complex (Table 9). Figure 4 presents a good relationship between β_{tot} values and dielectric constants.

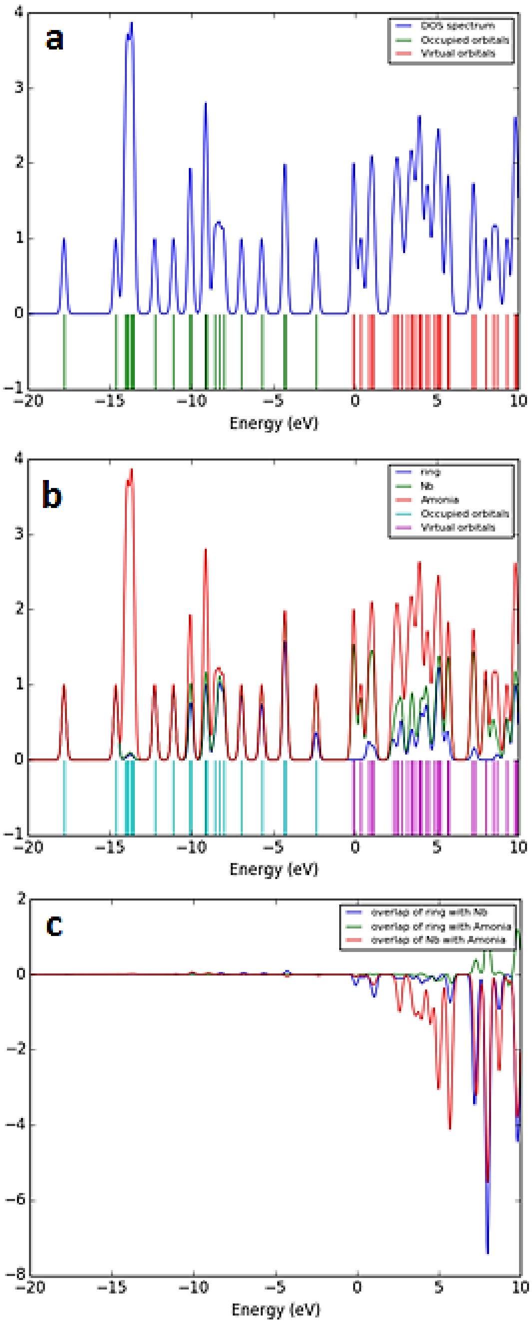

Fig. 3. (a) The calculated total electronic density of states (DOS) diagrams, (b) the calculated partial electronic density of states diagrams (PDOS), and (c) crystal orbital overlap population (COOP) for niobapyrimidinium complex.

Table 8. β components and β_{tot} values (10^{-30} esu) for *para*-substituted niobapyrimidinium

	H	F	Cl	Br	Me	NH_2	OH	Ome	CN	CHO	NO_2
β_{XXX}	591.69	806.91	877.82	907.44	-1.07	-41.76	2.09	-8.43	129.10	82.00	-56.40
β_{XXY}	2.34	0.72	-0.77	-1.11	-13.74	62.75	-14.29	17.60	0.02	0.25	1.55
β_{XYY}	487.71	470.44	468.04	478.02	-0.51	-7.29	1.80	-2.16	32.43	9.50	-13.30
β_{YYY}	-3.67	-3.37	-3.25	-3.55	33.29	109.09	-33.86	59.38	0.15	0.19	2.04
β_{XXZ}	-30.87	-14.84	-15.79	-16.77	-691.79	-697.92	-669.45	-707.97	-592.00	-616.79	-624.00
β_{XYZ}	-0.79	1.51	1.38	-1.83	1.98	-6.59	-0.26	3.41	0.60	0.01	7.67
β_{YYZ}	18.35	18.40	18.62	19.37	-487.76	-544.34	-518.83	-420.77	-446.00	-466.84	-440.00
β_{XZZ}	674.40	625.92	642.48	667.10	0.05	16.55	27.65	5.13	-41.30	20.33	34.93
β_{YZZ}	-2.00	-1.20	-1.51	-1.62	-4.56	186.03	2.88	154.22	-2.77	0.57	-3.26
β_{ZZZ}	79.73	74.10	75.59	79.30	-646.67	-1107.76	-907.10	-676.45	-615.00	-375.51	-65.70
β_{tot}	1.512E-29	1.65E-29	1.72E-29	1.77E-29	1.58E-29	2.05E-29	1.81E-29	1.57E-29	1.43E-29	1.26E-29	9.76E-30
$\beta_{tot} \times 10^{30}$	15.16	16.46	17.19	17.75	15.78	20.54	18.11	15.72	14.32	12.64	9.76

Table 9. β components and β_{tot} values (10^{-30} esu) for niobapyrimidinium in different media by using the PCM model

	DiEthylEther	Aniline	DiChloroMethane	Quinoline	DiChloroEthane
β_{XXX}	684.11	596.28	522.41	-522.47	454.85
β_{XXY}	-1.96	-0.17	-2.28	1.21	-1.02
β_{XYY}	513.36	419.61	398.05	-396.56	380.85
β_{YYY}	0.35	2.10	0.85	-0.30	-0.13
β_{XXZ}	-3.96	-2.25	-2.00	2.54	-2.67
β_{XYZ}	-5.63	-0.91	0.41	-0.37	16.73
β_{YYZ}	-0.38	-0.79	-0.16	0.38	0.38
β_{XZZ}	459.77	418.72	358.09	-360.25	310.14
β_{YZZ}	0.47	0.61	-0.02	-0.38	-0.42
β_{ZZZ}	-1.36	-0.49	0.64	0.98	0.17
β_{tot}	1.434E-29	1.24E-29	1.10E-29	1.10E-29	9.90E-30
$\beta_{tot} \times 10^{30}$	14.32	12.39	11.05	11.05	9.90

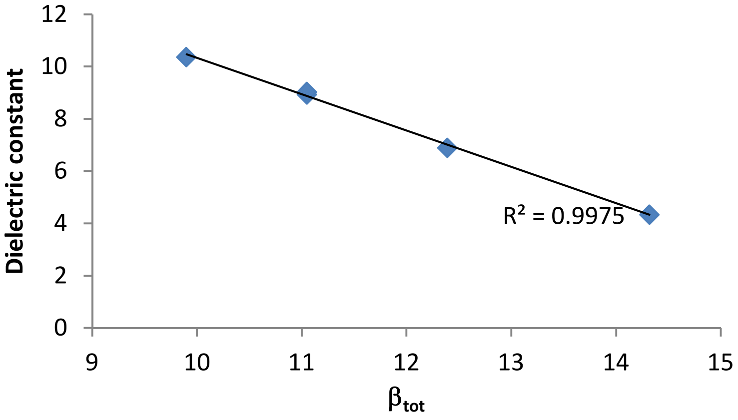

Fig. 4. Linear relationship of dielectric constants values with β_{tot} in niobapyrimidinium complex.

CONCLUSION

The *para*-substitution effect in niobapyrimidinium complex shows that:

- HOMO and LUMO energies of electron withdrawing substituents (X=CN, CHO, NO_2), are lower than donor electron substituents. Also, donor electron groups have less hardness, chemical potential and electrophilicity index rather than withdrawing electron groups.
- NICS calculation shows that niobapyrimidinium has π-aromaticity.
- There is largest β_{tot} values in X=NH_2 complex.

On the other hand, the study of solvent effect for niobapyrimidinium complex indicated:

- Absolute energies decrease with the increasing dielectric constants of solvents. On the other hand, ΔE_{solv} values indicate to increasing of stability in more polar solvents.
- Hyperpolarizability values show increasing of β_{tot} values by decreasing of dielectric constants
- These values show that d(CN) and d(CC)increases with increasing of dielectric constant of solvent.
- The values of HOMO energy are stabilized, with respect to the corresponding values in vacuum. But, the energies of LUMO in solvated media are destabilized rather than gas phase.

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