Effects of Substituent and Temperature on the Electronic Properties and Thermodynamics Parameters of 1-(Benzothiazolylamino) Methyl-2-Naphthol: A Computational Study

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Abstract

The effects of substituent and temperature on the 1-(benzothiazolylamino)methyl-2-naphthol molecules were studied at the CAM-B3LYP/6-311G(d,p) level of theory. Selected substituents were NH_2, OH, Me, F, Cl, CHO, COOH, CN and NO_2. Substituent effect on the frontier orbitals energies, HOMO-LUMO gap, chemical potential, and electrophilicity was explored. Dependencies of energy changes, reactivity properties and thermodynamic parameters (ΔG, ΔH and ΔS) on the Hammett's constants (σ_P) were provided. Thermodynamic parameters of the formation reaction were studied at 100-1000 K range.

Keywords: 1-(Benzothiazolylamino)methyl-2-naphthol, Substituent effect, Temperature effect, Thermodynamics parameters

INTRODUCTION

Using an effective and completely green process, 1-(benzothiazolylamino) methyl-2-naphthol derivatives have been synthesized through multi-component, one pot condensation reaction of 2-naphthol, 2-aminobenzothiazole, and aromatic aldehydes in the presence of maltose under solvent-free conditions[1]. This technique has several benefits such as mild conditions, high yields, clean reaction profile, simple operation, being ecologically friendly, and simple work-up. Multi-component reactions (MCRs) are significant in combinatorial chemistry since they can be suitably

used for synthesizing small drug-like molecules with structural diversity. These reactions allow compound synthesis in few steps, usually in one pot[2]. The benefits of these reactions are: being cheap, simple, and time and energy-saving with high bond-forming effectiveness[3]. Consequently, many studies have been done for developing new MCR. This method deals with an efficient way for the synthesis of 1-(benzothiazolylamino)methyl-2-naphthols by one-pot three-component reaction of 2-naphthol, 2- aminobenzothiazole, and aromatic aldehydes in the presence of maltose under solvent-free conditions because of the biological activity of 2-aminobenzothiazoles, and as a part of my ongoing project on MCR[4,5]. In another investigation, $NH_3(CH_2)_5NH_3BiCl_5$ was employed   as a new hybrid and efficient catalyst for the synthesis of 1- (benzothiazolylamino)methyl-2-naphthol derivatives under solvent-free conditions [6].

Substituent effect is significantly involved in chemistry. It has been reported that changes in the electron-donating groups (EDGs) and electron-withdrawing groups (EWGs) of molecules influence the performance of molecules. Many studies indicated the substituent effects on different physical and chemical features. For instance, substituent effects influence the thermal properties[7-9], molecular conformations [10], the rates of nucleophilic substitutions and elimination reactions [11], framework of material science [12,13], absorption bands of electronic spectra [14- 16] and NMR chemical shifts[17-20]. Useful relationships between the electronic and structural characteristics can be afforded by quantum chemical investigations [21-26]. That is why various computational investigations have reported substituent influence on the structural, electronic, and spectroscopic properties of organometallic complexes [27- 34]. Additionally, it is believed that quantitative substituent parameter scales are useful for explaining the polar or steric impact of the substituent on molecular features. For example, Hammett constant (σ_p) [35] defined the electronic effects of substituents on the equilibrium and rate constants of a reacting molecule. Also, quantum mechanics methods are useful tools for illustration of the electronic properties of molecules and thermodynamic parameters of reaction [36- 43].

Although synthesis and spectroscopic properties of the 1-(benzothiazolylamino) methyl-2-naphthol compound has been reported [6], reactivity and thermodynamic parameters of the formation reaction have been not investigated. Therefore, here, I report a computational study on the impact of substitution and temperature on the energy change, dipole moment, frontier orbital energy, reactivity features, and thermodynamic parameters in the preparation of 1-(benzothiazolylamino)methyl-2-naphthol by quantum chemical calculations.

COMPUTATIONAL METHODS

Optimization and vibrational analysis were done with Gaussian 09 software package[44]. The standard 6- 311G(d,p) basis set [45-48] was considered for the elements, respectively. CAM-B3LYP functional was used for the geometry optimization of the compound [49-51]. This functional is Handy et al's long range corrected version of B3LYP using the Coulomb-attenuating method [52]. The identities of the optimized structures as an energy minimum were confirmed by vibrational analysis.

RESULTS AND DISCUSSION

Energetic Aspects Figure 1 presents the reaction for preparing 1- (benzothiazolylamino) methyl-2-naphthol molecules. The energy changes of the studied reaction in the presence of EDGs and EWGs are calculated as:

$$\Delta E \text{ (reaction)} = [E(P) + E(H_2O)] - [E(R_1) + E(R_2) + E(R_3)] \qquad (1)$$

ΔE values are shown in Table 1. These values show the negative ΔE (reaction) values in the studied reactions. It can be observed the more negative values in the presence of EWGs compared to EDGs. There is a good linear correlation between ΔE (reaction) values and Hammett constants (Fig. 2):

$$\Delta E \text{ (r)} = -3.5866 \, \sigma_p - 3.2093; \ R^2 = 0.9900; \qquad \text{relation 1}$$

As shown, ΔE values are higher in the presence of EDGs compared to EWGs.

Thermodynamic Parameters

The values of the free energy enthalpy and entropy changes (ΔG, ΔH and ΔS, respectively) are calculated according to the following equation:

$$\Delta X \text{ (reaction)} = [X(P) + X(H_2O)] - [X(R_1) + X(R_2) + X(R_3)]; \ X = H, G, S \qquad (2)$$

The calculated parameters are listed in Table 1. The positive ΔG and negative ΔH values of the studied reactions reveal that these reactions are non-spontaneous and exothermic, respectively. There is a good linear correlation between ΔE values and Hammett constants:

$$\Delta G(r) = -3.3857\ \sigma_p + 12.692;\ R^2 = 0.9889; \qquad \text{relation 2}$$

$$\Delta H(r) = -3.5149\ \sigma_p - 0.9954;\ R^2 = 0.9882; \qquad \text{relation 3}$$

Higher ΔG values are observed in the presence of EDGs compared to EWGs. In addition, more exothermic reactions are shown in the presence of EWGs compared to EDGs. The negative ΔS values of these reactions are expectable, because, formation of one molecule from two interacting molecules decreases entropy of the reaction

Dipole Moment

The dipole moment is a parameter widely used to quantify polarity of molecules and measures polarity of covalent bonds. This parameter was calculated as the product of the charges localized on the atoms and the distances between them. In addition, the total (static) value of this parameter was computed as:

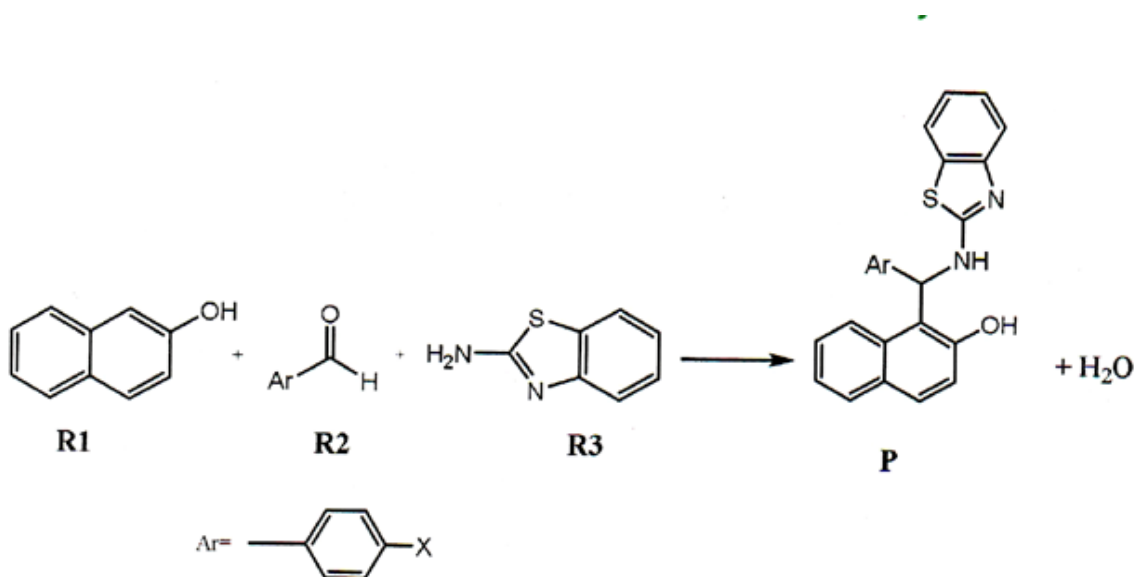$$\mu_{tot} = \sqrt{\mu_x^2 + \mu_y^2 + \mu_z^2} \qquad (3)$$

Fig. 1. The preparation reaction of 1-(benzothiazolylamino) methyl-2-naphthol molecules (X = NH₂, OH, Me, H, F, Cl, CHO, COOH, CN and NO₂)

Table 1. Changes of Energy (ΔE, kcal mol^{-1}), Ffree Eenergy (ΔG, kcal mol^{-1}) and Eentropy (ΔS, cal mol^{-1} K^{-1}) of 1-(Benzothiazolylamino) Methyl-2- naphthol Molecules Formation at CAM-B3LYP/6-311G(d,p) Level of Theory. σ_p is Hammett's Constant

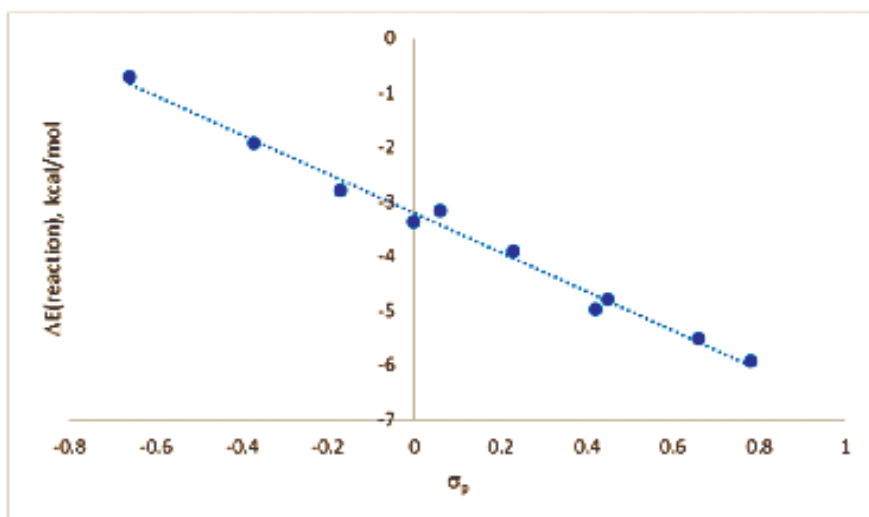| X	σ_p	ΔE	ΔG	ΔH	ΔS
NH$_2$	-0.66	-0.71	15.05	1.51	-45.43
OH	-0.37	-1.92	13.80	0.24	-45.48
Me	-0.17	-2.79	13.32	-0.60	-46.69
H	0.00	-3.37	12.43	-1.20	-45.73
F	0.06	-3.17	12.76	-0.96	-46.01
Cl	0.23 -	3.91	11.86	-1.68	-45.41
CHO	0.42	-4.98	11.14	-2.73	-46.52
COOH	0.45	-4.80	11.16	-2.56	-46.02
CN	0.66	-5.52	10.66	-3.24	-46.61
NO$_2$	0.78	-5.92	10.00	-3.65	-45.78

Fig. 2. Linear correlation between ΔE (reaction) values and Hammett constants.

Table 2. Total Dipole Moment (μtot, Debye), Frontier Orbitals Energies (eV), HOMO-LUMO Gap (eV), Hardness (eV), Chemical Potential (μ, eV), and Electrophilicity (ω, eV) of 1-(Benzothiazolylamino) methyl-2-naphthol Molecules at CAM-B3LYP/6-311G(d,p) Level of Theory

X	μtot	E(HOMO)	E(LUMO)	Gap	η	μ	ω
NH_2	4.33	-6.81	-0.23	6.58	3.29	-3.52	1.89
OH	2.87	-6.91	-0.31	6.60	3.30	-3.61	1.97
Me	4.19	-6.89	-0.30	6.59	3.29	-3.60	1.96
H	4.12	-6.92	-0.33	6.59	3.29	-3.62	1.99
F	4.51	-7.00	-0.40	6.60	3.30	-3.70	2.08
Cl	4.77	-7.04	-0.44	6.60	3.30	-3.74	2.12
CHO	6.62	-7.08	-0.53	6.54	-3.80	2.21	3.27
COOH	5.66	-7.03	-0.43	6.59	3.30	-3.73	2.11
CN	6.80	-7.17	-0.56	6.61	3.31	-3.87	2.26
NO^2	6.81	-7.19	-1.13	6.07	3.03	-4.16	2.85

where μ_x, μ_y and μ_z are dipole moment along x, y and z axes. Table 2 lists the calculated dipole moment values of the molecules. These values show that presence of the EWGs induces a larger dipole moment compared with the EDGs.

Molecular Orbital Analysis

Table 2 shows the frontier orbital energy, HOMOLUMO gap, hardness, electrophilicity and chemical potential values of the molecules formed. As shown, frontier orbitals are stabilized in the presence of EWGs, whereas, these orbitals are destabilized in the presence of EDGs. There is a good linear correlation between the HOMO energy values:

E(HOMO) = -0.2587σ_p - 6.9676; R² = 0.9221;   relation 4

This behavior is due to an electron-withdrawing inductive effect which concentrates the electronic density over the substituted region of the compound.

This correlation may be used for predicting E(HOMO) for other substituents for which σp is known. The same correlation is not observed for both E(LUMO) energies, since the LUMO energy in the presence of NO2 group is lower than the other groups by about 0.6 eV. In addition, these values reveal that HOMO-LUMO gap values are higher in the presence of EDGs than EWGs.

As shown in Fig. 3, plotting the energies of the frontier orbitals of the molecules investigated in this paper seems to be reasonable. The linear interpolation of the data points matching the studied molecules yields a correlation coefficient of 0.6837. I notice that the data point matching with CHO, COOH and NO_2 substituents are located far apart from the straight line. In these derivatives, either the HOMO or the LUMO differs in topology regarding other substituents, as revealed in Fig. 3a. Thus, by excluding the frontier orbitals' energies of CHO, COOH and NO_2 substituents, the excellent correlation coefficient of 0.9982 is obtained as shown in Fig. 3b. Figure 4 shows the plots of frontier orbitals for X = H, CHO, COOH and NO_2 substitutions. As shown, plots of HOMO are similar in the presence of these substituents and the maximum contribution of atomic orbitals in HOMO is concentrated on the benzothiazolylamino ring. In the presence of X = NO_2 and CHO substituents, the maximum contribution of atomic orbitals in LUMO is concentrated on the aryl ring. Nevertheless, in the presence of other substituents, the maximum contribution of atomic orbitals in LUMO is concentrated on the naphthol ring.

η, μ and ω are global hardness, chemical potential and electrophilicity. They are defined as global reactivity descriptors[53-56] and determined based on Koopman's theorem [57]. These values for these molecules are calculated by the following equations:

$$\eta = \frac{E(LUMO) - E(HOMO)}{2} \tag{4}$$

$$\mu = \frac{2\, E(HOMO) + E(LUMO)}{2} \tag{5}$$

$$\omega = \frac{\mu^2}{2\eta} \tag{6}$$

As shown, chemical potentials are greater in the presence of EDGs than EWGs. On the other hand, there are higher electrophilicity values in the presence of EWGs than EDGs

TEMPERATURE EFFECT

Temperature effect on the thermodynamic parameters in the presence of X = H are listed in Table 3. As shown, the positive $\Delta G°$ and negative $\Delta H°$ values of the studied reaction are at 100-1000 K range. The molecular vibration intensities enhance with increasing temperature, so, thermodynamic functions increase at any temperatures from 100 to 1000 K for the studied compound. There are good linear correlations between $\Delta G°$ and $\Delta H°$ values with temperature:

$\Delta G° = 0.0516T + 2.7721;$ $R² = 0.9997;$ relation 5

$\Delta H° = 0.0033T + 1.4141;$ $R² = 0.9979;$ relation 6

Furthermore, the negative $\Delta S°$ values of the reaction are expectable in the studied range of temperature. The $\Delta S°$ values are increased with increasing the temperature. There is a good linear correlation between $\Delta S°$ values and temperature:

$\Delta S° = 0.0074T - 55.914;$ $R² = 0.9194;$ relation 7

These relations can be employed for predicting thermodynamic parameters for other temperatures.

CONCLUSIONS

Computational investigation of the substituents and temperature influences on the formation reaction of 1-(benzothiazolylamino) methyl-2-naphthol showed the negative ΔE values for the reactions. Calculated dipole moment values revealed that EWGs induce a larger dipole moment compared to EDGs. Higher negative values were found in the presence of EWGs compared to EDGs. Frontier orbitals were stabilized in the presence of EWGs, whereas, these orbitals were destabilized in the presence of EDGs. Thermodynamic analysis revealed that these reactions were non-spontaneous and exothermic. The ΔG and negative ΔH values were increased with increasing the temperature.
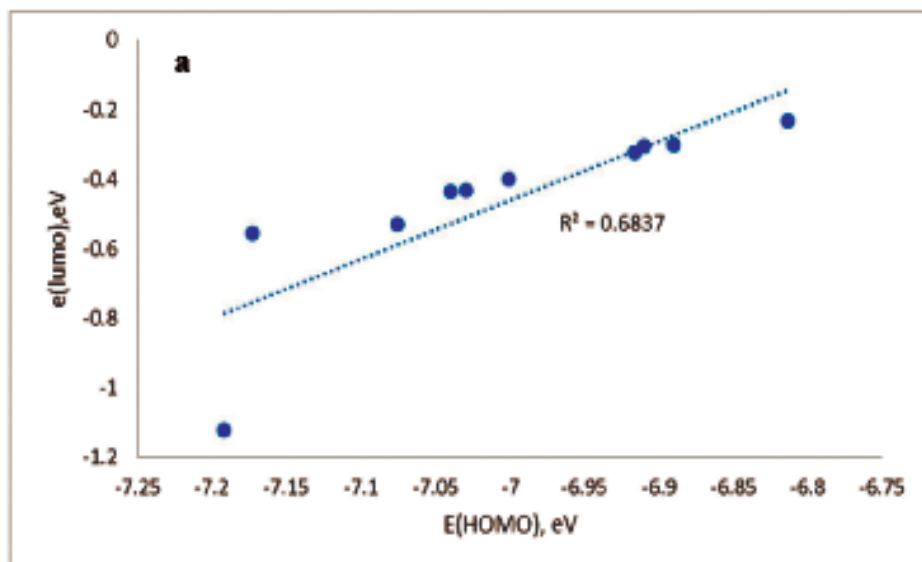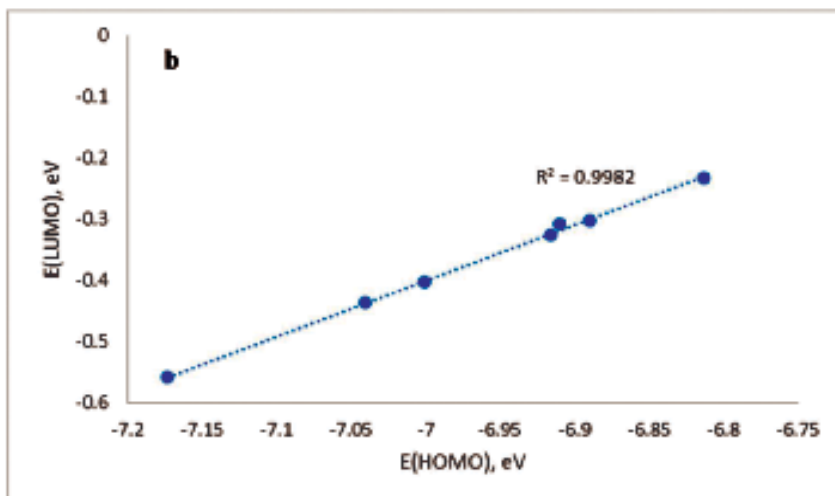
Fig. 3. Correlations between E(HOMO) and E(LUMO) in the presence of (a) all substitutions and (b) X = NH₂, OH, Me, H, F, Cl, and CN) substitutions.

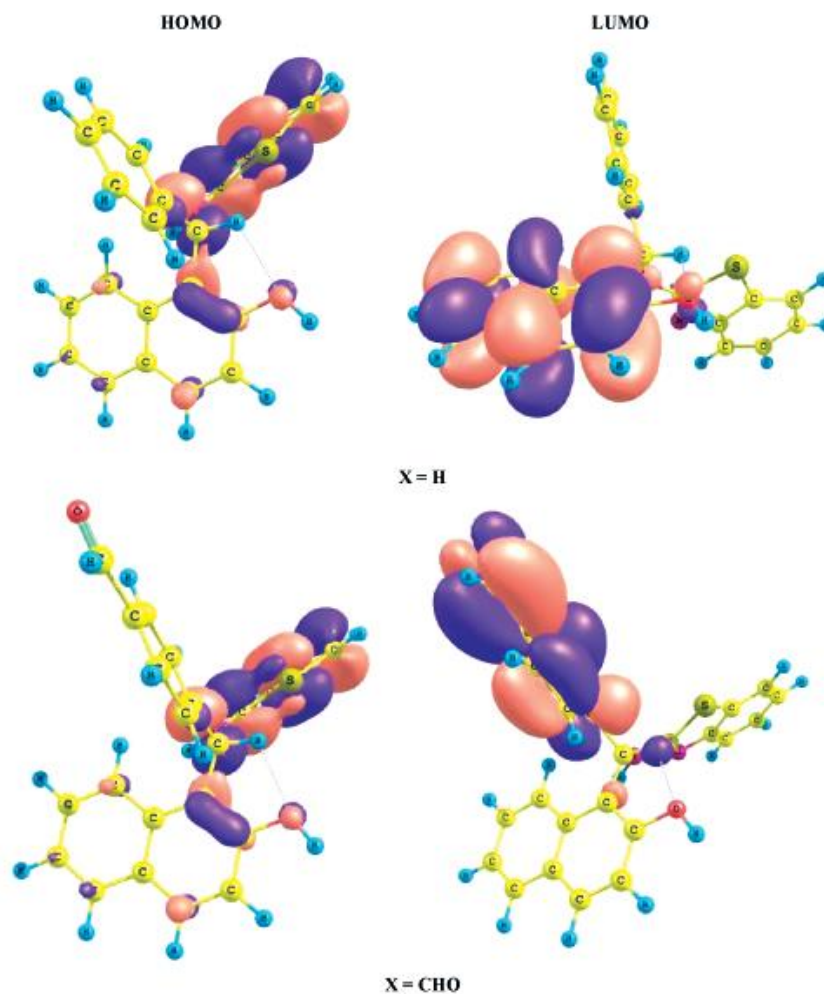*Fig. 4. Plots of frontier orbitals in the presence of X = H, CHO, COOH, NO₂ substitutions*

Table 3. Changes of Free Energy ($\Delta G^{\bullet}$, kcal mol^{-1}), Enthalpy ($\Delta H^{\bullet}$, kcal mol^{-1}) and Entropy ($\Delta S^{\bullet}$, cal mol-1 .K^{-1}) of the Formation of 1-(Benzothiazolylamino) Methyl-2- naphthol Molecules with Temperature at CAM-B3LYP/ 6-311G(d,p) Level of Theory

X	ΔG°	ΔH°	ΔS°
100	7.46	1.80	-56.65
200	12.99	2.13	-54.30
300	18.36	2.40	-53.18
400	23.63	2.69	-52.35
500	28.83	3.01	-51.64
600	33.96	3.35	-51.03
700	39.04	3.70	-50.48
800	44.06	4.06	-50.00
900	49.04	4.42	-49.58
1000	53.98	4.79	-49.19

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