



## Investigation of Theoretical Calculations of 2-(1-Phenylethylideneamino) Guanidine Compound: NBO, NLO, HOMO-LUMO and MEP Analysis by DFT Method

*2-(1-Phenylethylideneamino) Guanidine Bileşiminin NBO, NLO, HOMO-LUMO and MEP Analizlerinin DFT Metodu Kullanılarak Teoriksel Hesaplamalar ile İncelenmesi*

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### Abstract

In this study exhibits the characterization of 2-(1-Phenylethylideneamino) guanidine compound has been investigated using quantum chemical calculations. The molecular geometry of 2-(1-Phenylethylideneamino)guanidine in the ground state is optimized by using DFT method with 6-311G+(d,p) basis set. The natural bond orbital and Mulliken atomic charge distribution analysis confirm intramolecular charge transfers and intramolecular interactions. The Frontier molecular orbitals are drawn, and the related global quantities: electronic chemical potential, electrophilicity index, HOMO and LUMO energy eigenvalues are calculated and discussed at B3LYP/6-311+G(d,p) level of theory. Further, molecular electrostatic potential contour map (MEP) is simulated and nonlinear optical properties (NLO) has been calculated at the same level of the theory.

**Keywords:** Guanidine, HOMO and LUMO, MEP, NBO, NLO

### Öz

Bu çalışma 2-(1-Feniletildenamino) guanidin bileşiminin karakterizasyonu kuantum kimyasal hesaplamalar kullanılarak sunulmaktadır. 2-(1-Feniletildenamino) guanidin bileşiminin taban durumundaki moleküler geometrisi DFT metodu ile 6-311G+(d,p) baz seti kullanılarak optimize edilmiştir. Molekülün doğal bağ orbital ve Mulliken atomik yük dağılım analizleri moleküller arası yük transferini ve moleküller arası etkileşimleri doğrulamaktadır. Sınır moleküler orbitalleri çizilmiş ve HOMO ve LUMO enerji özdeğerleri B3LYP/6-311+G(d,p) seviyesinde hesaplanmış ve tartışılmıştır. İlave olarak, moleküler elektrostatik potansiyel kontör haritası (MEP) çizilmiş ve lineer olmayan optiksel özellikler (NLO) 6-311+G(d,p) baz seti kullanılarak hesaplanmıştır.

**Anahtar Kelimeler:** Guanidin, HOMO ve LUMO, MEP, NBO, NLO

### 1. Introduction

Guanylhyazones (alkylenaminoguanidines, carboximideamide hydrazones, diaminomethylene hydrazones) are condensation products of oxo compounds with aminoguanidines. This class of compound has been interested to researchers for a long time (Thiele 1892) due to a wide variety of pharmacological applications found for many representatives (Richter et al. 1993, Schleuder et al. 1993). Further, guanylhyazones are valuable synthetic building blocks for ring closure reactions which lead to several nitrogen-containing heterocycles (Sarıpınar et al. 2005). Protomeric tautomerism is of much interest in experimen-

tal as well as theoretical chemistry since it is an important reaction in biological processes. Guanylhyazones can exist in two tautomeric forms ( Zoltan et al. 1999). They may undergo proton shifts (tautomerism) rapidly and easily, and the chemical reactivity of the two isomers may be quite different.

On the other hand, it is well known that the density functional theory (DFT), a quantum chemical calculation method, has been widely used to determine the molecular geometry and electronic properties (HOMO, LUMO, NLO, and MEP) of polyatomic molecules. In the present study, we used the DFT approach in order to perform which included exchange correlation functions and allowed us to obtain accurate electron density from the Kohn-Sham equations (Kohn 1965, Handy et al. 1993). Namely, the structural, electronic and NLO properties of the title

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compound are investigated by using DFT calculations. Previously, this compound was synthesized (Demir et al. 2006) and its crystal structure determination was carried out by single-crystal X-ray diffraction method (Demir et al. 2006).

## 2. Materials and Method

All calculations for the studied single crystal data were carried out using Gaussian 09 software (Frisch et al. Gaussian 09 2009). The geometries were optimized by minimizing the energies with respect to all the geometrical parameters without imposing any molecular symmetry constraints. The molecular structure optimization of the compound and corresponding electronic properties were calculated using DFT-B3LYP exchange correlation functional (Lee et al. 1988, Stephens et al. 1994, Devlin et al. 1995) employing 6-311+G(d,p) basis set as implemented in Gaussian 09 package (Frisch et al. Gaussian 09 2009). The GaussView program was used for the molecular visualization of the calculated structure.

As the ( $\alpha$ ) and  $\beta_{\text{total}}$  values of Gaussian output were in atomic units (a.u.), they have been converted into electrostatic units (esu) ( $\alpha$ ; 1 a.u. =  $0.1482 \times 10^{-24}$  esu,  $\beta$ ; 1 a.u. =  $8.6393 \times 10^{-33}$  esu). The band gaps of the electronic properties such as frontier molecular orbital HOMO and LUMO energies were determined by the DFT/B3LYP approach, while the natural bonding orbital (NBO) calculations (Glendening et al. 2011) were determined using the Gaussian 09 package. The calculations for both electronic properties and NBO were done at the same level in order to better understand various second order interactions between the filled orbitals of one subsystem and the vacant orbitals of the other subsystem, which determine the intra/intermolecular delocalization or hyperconjugation. These calculations allow us to analyze probable charge-transfers and intermolecular bond paths.

## 3. Results

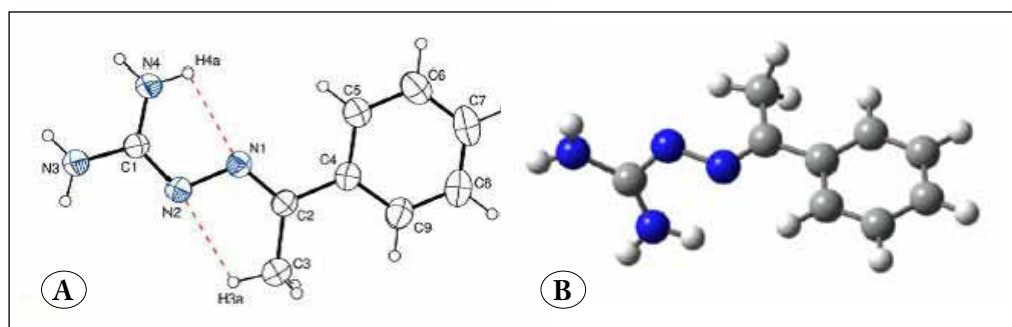
### 3.1. Optimized Geometry

Density Functional Theory (DFT) with Gaussian-09 program package employing B3LYP (Becke three parameter Lee-Yang-Parr) method with 6-311+G(d,p) basis set is used to designate optimized geometric parameters. Both Molecular and optimized structure showing the atomic numbering scheme is shown in Figure 1(a) and (b). The crystallographic details which are required for establishing the molecular structure were investigated in a former study (Demir et al. 2006). In the aminoguanidine group, the N—N bond length is 1.401(2) Å (Demir et al. 2006), corresponding to a pure single bond 1.41 Å (Burke-Laing and Laing 1976). That the lone-pair electrons on atom N2 are delocalized through conjugation with the amidine group, rather than the N1=C2 double bond, is also seen in the C1—N2 bond length of 1.317(3) Å (Demir et al. 2006), which is intermediate between a single and a double bond, and similar to the two C—N bonds in the amidine group. Theoretically, these bond lengths were calculated at 1.382 Å (N—N) and 1.301 Å (C1—N2). Table 1 compares experimental data with data obtained by the theoretical study which reveals that all optimized bond lengths and bond angles are slightly larger than the experimental values.

The data obtained in the theoretical study is created in the gas phase and molecular interactions are not considered at this stage, whereas the experimental data is acquired in the solid state and in which crystal field interactions, e.g. Van der Waals forces, crystal packing force and hydrogen bond interactions. For this reason, the differences between the theoretical and experimental results may be attributed to the different environments of the molecule.

### 3.2. Frontier Molecular Orbitals (FMOs), Electronic Descriptors and Molecular Electrostatic Potential Surface (MEPS)

Molecular electrical properties are designated by energy gap



**Figure 1.** (A) The molecular structure of the 2-(1-Phenylethylideneamino) guanidine molecule, showing the atom-numbering scheme (Demir et al. 2006) (B) The theoretical geometric structure of title compound.

between HOMO and LUMO orbitals. At the same time, these gap is a measure of electron conductivity.

Highest occupied molecular orbital energy signalizes an electron's ability to give while the lowest unoccupied molecular orbital energy signalizes an electron's feat to acknowledge, and the energy gap describes the chemical reactivity and kinetic stability of the molecules. It can be seen that from the Figure 2, the HOMO is located over nitrogen and carbon atoms; from the HOMO orbital to LUMO orbital transition means an electron density transfer to nitrogen to carbon atoms in the ring. The HOMO-LUMO energy gap of 2-(1-Phenylethylideneamino) guanidine calculated at the DFT/B3LYP method with 6-311+G(d,p) level is shown in Figure 2 and it reveals that the energy gap reflects the chemical activity of the molecule. The narrow energy gap between HOMO and LUMO energies is profitable intramolecular charge transfer. It makes the material NLO active.

**Table 1.** Some optimized and experimental geometries parameters of 2-(1-Phenylethylideneamino)guanidine in the ground state.

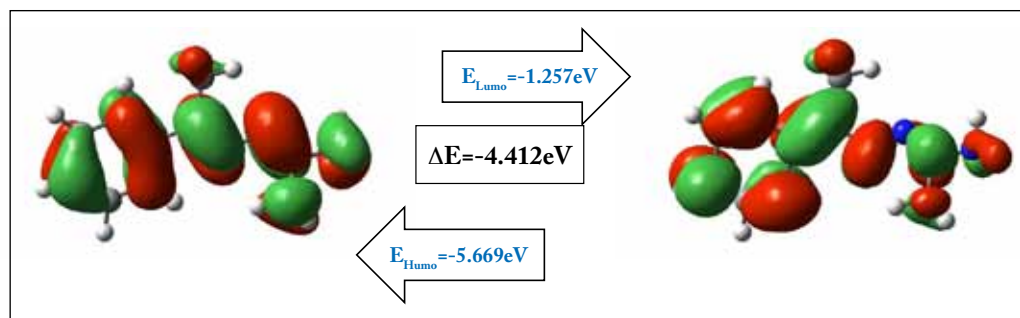
Bond Lengths(Å)	X-ray <sup>b</sup>	DFT
C1—N2	1.317 (3)	1.301
C1—N4	1.335 (3)	1.373
C1—N3	1.354 (3)	1.382
C2—N1	1.286 (2)	1.291
N1—N2	1.401 (2)	1.382
RMSE <sup>a</sup>	0.023	
Max. difference <sup>a</sup>	0.038	
Bond Angles(°)	X-ray <sup>b</sup>	DFT
N4—C1—N3	117.1 (2)	115.828
N1—C2—C4	116.4 (2)	116.960
C2—N1—N2	116.41 (17)	116.914
RMSE <sup>a</sup>	0.85	
Max. difference <sup>a</sup>	1.272	

<sup>a</sup>RMSE(Root Mean Square Error) and the maximum difference between theoretical and experimental results(X-ray diffraction). <sup>b</sup>(Demir et al. 2006).

The molecular electrostatic potential (MEP) map assists to imagine positive and negative charged regions of a molecule. There with it is qualitatively used as a probe for placement the reactive sites in a molecule. By operating MEP maps, at the begging, we can perceive to which an electrophile and nucleophile would be attracted. This pictural method has been found to be a very useful tool to examine the connection between the molecular structure and the physiochemical specialty relation of molecules including biomolecules and drugs (Murray and Sen 1996, Alkorta and Perez 1996, Scrocco and Tomasi 1978, Luque et al. 1993, Sponer and Hobza 1996, Gadre and Shrivastava 1991). These surface of 2-(1-Phenylethylideneamino)guanidine was calculated by B3LYP/6-311+G(d,p) level. In this way, the title compound was comprehended the relative polarity. This map looks like a rainbow which was consist of colors of the electromagnetic spectrum. In this map, the red and blue regions hint to the electron rich and electron poor region respectively. On the other hand, the slightly electron rich region is indicated by yellow and the green region in MEP proposes a nearly neutral region. It is evident from the MEP map (Figure 3) that the region around the hydrogen atoms of the carbon atoms is electron deficient (light blue color), therefore a binding site for electrophiles. The region around the nitrogen atoms corresponding to the N-N group represents the most electron rich region. The while is the binding site which is called as nucleophiles.

### 3.3. Natural Bond Orbital (NBO) Analysis

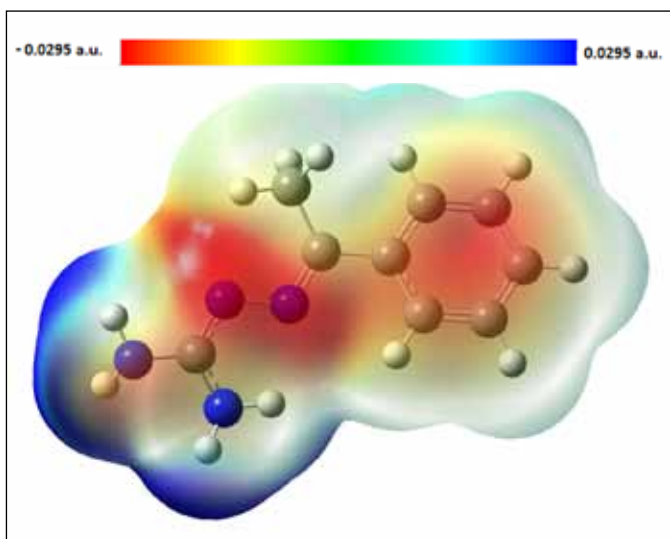
NBO analysis was conducted on the molecule at the DFT/B3LYP/6-311+G(d,p) level in order to explain the intramolecular, hybridization and delocalization of electron density ( $E_D$ ) within the molecule which is presented in Table 2. NBO analysis provides an efficient method for studying intra- and intermolecular bonding and interaction among bonds and also provides the basis for investigating charge transfer or conjugative interaction in molecular systems (Snehalatha et al. 2009). The large  $E^{(2)}$  value indicates the



**Figure 2.** Energy levels and the 3D plots of the HOMO and LUMO of the title compound at the B3LYP/6-311+G(d,p) level.

more intensive interaction between electron donors and electron acceptors.

The intramolecular hyperconjugation interactions display  $\pi(\text{C7-C8}) \rightarrow \pi^*(\text{C4-C9})$ ,  $\pi^*(\text{C4-C9})$  [ $E_D=0.36989e$ ,  $0.30024e$ ,  $E^{(2)}= 19.76, 19.05 \text{ kJ/mol}^{-1}$  with B3LYP level],  $\pi(\text{C4-C9}) \rightarrow \pi^*(\text{C7-C8})$ ,  $\pi^*(\text{C5-C6})$ ,  $\pi^*(\text{C2-N1})$  [ $E_D=0.33276e$ ,  $0.30024e$ ,  $0.200351e$ ,  $E^{(2)} = 20.67, 19.04, 15.42 \text{ kJ/mol}^{-1}$  with B3LYP level] and  $\pi(\text{C5-C6}) \rightarrow \pi^*(\text{C7-C8})$ ,  $\pi^*(\text{C4-C9})$  [ $E_D=0.33276e$ ,  $0.36989e$ ,  $E^{(2)}= 20.45, 19.39 \text{ kJ/mol}^{-1}$  with B3LYP level] leading



**Figure 3.** MEP maps of the title compound of calculated at B3LYP/6-311+G(d,p).

to stabilization of the phenyl ring. NBO analysis clearly explains the evidence of the formation of a weak H-bonded interaction between the LP(N) and  $\sigma^*(\text{C-C})$  and  $\sigma^*(\text{C-N})$  antibonding orbitals. Notwithstanding the energetic contribution for LP(1)N1  $\rightarrow \sigma^*(\text{C2-C3})$  ( $11.05 \text{ kJ/mol}^{-1}$ ) and LP(1)N1  $\rightarrow \sigma^*(\text{C1-N4})$  and LP(1)N2  $\rightarrow \sigma^*(\text{C1-N4})$  ( $13.01 \text{ kJ/mol}^{-1}$ ) of hyperconjugation interaction is weak, these  $E^{(2)}$  values are chemically significant and can be used as a measure of the intramolecular delocalization. According to our results, the intramolecular charge transfer [ $n \rightarrow \sigma^*$ ,  $n \rightarrow \pi^*$ ,  $\pi \rightarrow \pi^*$ ] occurs in the title compound.

### 3.4. NonLinear Optical Properties (NLO)

Theoretical calculations on molecular hyperpolarizability ( $\beta$ ) are quite useful in understanding the relationship between the molecular structure and nonlinear optical properties, however, hyperpolarizability is difficult task to measure directly computational calculation is an alternate choice (Kleinmann 1962). Urea is one of the prototypical molecules used in the study of the nonlinear properties of molecular systems. Therefore, it has been frequently used as a threshold value for comparative purposes. The first hyperpolarizability ( $\beta_0$ ) of this molecular system and related properties ( $\alpha_{\text{tot}}$  and  $\Delta\alpha$ ) are calculated at B3LYP/6-311+G(d,p) level and their calculated values are given in Table 3.

The dipole moment ( $\mu$ ) and the mean polarizability ( $\alpha_{\text{tot}}$ ) were calculated and they were found to be 2.039 D and  $2.371 \times 10^{-23}$  esu, respectively. Additionally, the first order

**Table 2.** Second-order perturbation theory analysis of Fock matrix in NBO basis for the title compound.

Donor(i)	Type	$E_D$ (i) (e)	Acceptor(j)	Type	$E_D$ (j) (e)	$E^{(2)a}$ ( $\text{kJ/mol}^{-1}$ )	$E(j)-E(i)^b$ (a.u.)	$F(i, j)^c$ (a.u.)
BDC7-C8	$\pi$	1.66846	BD* C4-C9	$\pi^*$	0.36989	19.76	0.29	0.068
			BD* C5-C6	$\pi^*$	0.30024	19.05	0.29	0.067
BDC4-C9	$\pi$	1.63955	BD* C7-C8	$\pi^*$	0.33276	20.67	0.28	0.068
			BD* C5-C6	$\pi^*$	0.30024	19.04	0.28	0.067
			BD* C2-N1	$\pi^*$	0.20351	15.42	0.28	0.061
BD C5-C6	$\pi$	1.67491	BD* C7-C8	$\pi^*$	0.33276	20.45	0.28	0.068
			BD* C4-C9	$\pi^*$	0.36989	19.39	0.28	0.067
BDN2-C1	$\pi$	1.88405	BD* C2-N1	$\pi^*$	0.20351	15.14	0.35	0.066
LP(1) N1	n	1.93082	BD* C2-C3	$\sigma^*$	0.03541	11.05	0.79	0.084
LP(1) N1	n	1.93082	BD* C1-N4	$\sigma^*$	0.04300	13.01	0.82	0.093
LP(1) N2	n	1.92994	BD* C1-N4	$\sigma^*$	0.04300	13.01	0.82	0.093
LP(1) N4	n	1.81470	BD* N2-C1	$\pi^*$	0.35975	38.37	0.32	0.104
LP(1) N3	n	1.83786	BD* N2-C1	$\pi^*$	0.35975	32.47	0.33	0.097
BD* N2-C1	$\pi^*$	0.35975	BD* C2-N1	$\pi^*$	0.20351	29.31	0.02	0.044

<sup>a</sup>  $E^{(2)}$  means energy of hyper conjugative interaction (stabilization energy).

<sup>b</sup> Energy difference donor and acceptor i and j NBO orbitals.

hyperpolarizability of these compound was found to be  $1.1011 \times 10^{-29}$  esu. Based on these results, we decide the title compound and its derivatives are an attractive object for future studies of nonlinear optical properties.

### 3.5. Mulliken Population Analysis

The Mulliken charge in any molecule is directly related to their vibrational properties and quantifies how the electronic structure charges under atomic displacement. Therefore it is directly related to the chemical bonds present in the title molecule. It affects many parameters of the molecule e. g. its polarizability, electronic structure, dipole moment and other properties of the molecular system (Govindarajan and Karabacak 2012, Govindasamy et al. 2014).

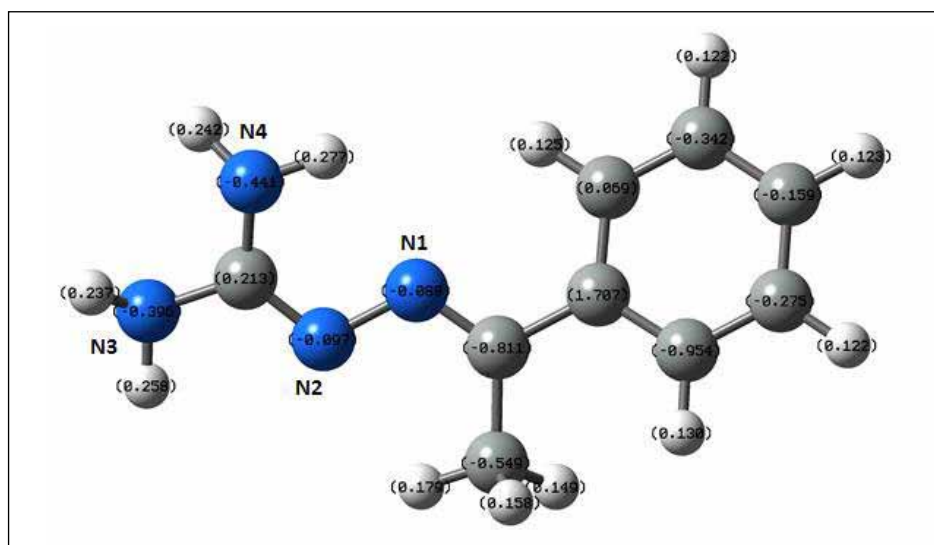
Analyzing the results, N3 and N4 atoms have larger negative atomic charges whereas H4a atom linking to N4 has larger positive atomic charge than other hydrogen atoms in gas-phase. This is due to N-H...N hydrogen bonds. The magnitude of the carbon atomic charges are found to be both positive and negative, in contrast, atomic charges of the hydrogen are found to be only positive.

### 4. Discussion and Conclusion

In this study, density functional calculations on 2-(1-Phenylethylideneamino)guanidine beginning from X-ray data have been performed. The molecular geometry, NBO analysis, NLO analysis of the title compound in the ground state were

**Table 3.** The molecular electric dipole moment  $\mu$  (Debye), polarizability  $\alpha$  ( $\times 10^{-24}$  esu) and hyperpolarizability  $\beta$  ( $\times 10^{-33}$  esu) values of this molecule and Urea.

Dipole Moment	Polarizability	First Hyperpolarizability
$\mu_x$ 1.843	$\alpha_{xx}$ 249.245	$\beta_{xxx}$ -1276.27
$\mu_y$ -0.4201	$\alpha_{yy}$ 145.082	$\beta_{yyy}$ 27.49
$\mu_z$ -0.767	$\alpha_{zz}$ 85.807	$\beta_{zzz}$ 12.80
$\mu_{tot}$ 2.039 D	$\alpha_{tot}$ $2.371 \times 10^{-23}$ e.s.u	$\beta_{tot}$ $1.1011 \times 10^{-29}$ e.s.u
	$\Delta\alpha$ 29044.72	$\beta_{xxx}$ -1276.27
		$\beta_{yyy}$ 27.49
		$\beta_{zzz}$ 12.80
		$\beta_{xyx}$ -108.09
		$\beta_{xyy}$ 27.49
		$\beta_{xzz}$ 78.10
		$\beta_{yxx}$ 62.83
		$\beta_{yzz}$ -15.70
		$\beta_{zxx}$ -22.51
		$\beta_{zyz}$ -23.12



**Figure 4.** Mulliken's atomic charges of the titled compound performed at the B3LYP/6-311+G(d,p) method.

investigated using DFT. The theoretically calculated values of both bond lengths and bond angles of the structures of the minimum energy were then compared with X-ray crystallographic data. NBO results inform the intramolecular charge transfer between bonding and antibonding orbitals. Atomic charges and the bond order have been investigated theoretically. Additionally, charge transfer between HOMO and LUMO energies and the energy gap between the orbitals were examined. A small HOMO-LUMO range is of great importance both in terms of intramolecular charge transfer and biological activity. When MEP map is examined, the negative regions on the surface were situated the N1 and N2 atoms while positive regions were enclosed onto NH<sub>2</sub>, CH<sub>3</sub> groups, and phenyl ring's hydrogens.

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