

Theoretical study of the geometrical and electronic properties of N, N'-di(Ortho-Substituted benzyl) Hydrazine.

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Abstract

In this paper, we report on a theoretical study of N, N'-di(ortho-substituted benzyl) hydrazine (DBH (R)). The conformational analysis, structural and electronic properties were performed by the method B3LYP/6-31G (d). This study aims to show the interest of the substitution of radicals (R) of the two benzyl groups, then its effect on the physico-chemical properties. The results show that the values of the bonds lengths and angles of the torsion of the compounds studied are comparable to those obtained in the literature. Inductive or mesomeric effect of the substituent (R) has an impact on the length of the bridge bond the N-N, energy Gap, maximum absorption and stability of these compounds.

Keywords: *N,N'*-di (ortho-substitued benzyl) hydrazine; Theoretical study; Conformational analysis, HOMO, LUMO.

1. Introduction

The formula N_2H_4 hydrazine is a colorless liquid. It is a reducing agent that breaks down slowly in air [1]. It is mainly used as treatment for deoxygenation corrosion in boilers and is used as rocket fuel and fuel cells [2]. Hydrazine is also a local irritant that is readily absorbed through the skin and by inhalation, potentially causing bronchitis and pulmonary edema [3]. In addition, it is suspected of being carcinogenic and a mutagenic compound [3]. In this study, we became interested in the theoretical study of N, N'-dibenzalhydrazine: $C_{14}H_{12}N_2$ (benzalazine (DBH)). This was synthesized according to the method used by Md. Mijanuddin. [4]. There is condensation of hydrazine and benzaldehyde in a molar ratio 1: 2 in methanol after filtration and washing with the same solvent. Single crystals of (DBH) of the

color yellow can be obtained by slow evaporation its solution in tetrahydrofuran. Figure 1 shows the diagram of N, N'-di (ortho-substituted benzyl) hydrazine.

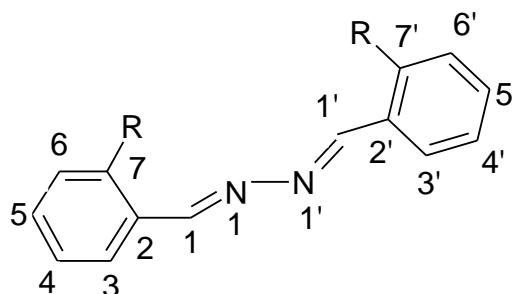


Figure 1: N, N'-di (ortho-substituted benzyl) hydrazine (DBH (R)) with R = H, Me, OH and OMe

2. Theoretical (DFT method)

To achieve this goal, methods of quantum mechanics are implemented to obtain structural and electronic energy descriptions of these compounds. The density functional theory (DFT) has become an essential tool for quantum chemistry for accurate modeling of molecular chemistry applicable [5].

2.1. Work Methodology

Geometries of N, N'-di (ortho substituted benzyl) hydrazine (DBH (R)) with R = H, Me, OH and OMe were optimized by density functional theory (DFT) using the hybrid method B3LYP with the basis 6-31G (d) [6]. The total optimized structure for each molecule is taken as the starting point for the conformational analysis, the twist angle θ ($-\text{C}=\text{N}-\text{N}=\text{C}-$) of the two phenyl groups varies from 0 to 180° by step of 20 degrees. All calculations were performed using the Gaussian 03 program [7] and the values of the absorption maxima were conducted by the semi-empirical ZINDO method [8].

3. Results and Discussion

3.1. Geometric optimization of the compounds DBH(R)

The optimization of different compounds was performed using the method B3LYP/6-31(d). The fully optimized geometries of molecules DBH (R) are shown in Figure 2.

The geometrical parameters of compounds DBH(R) obtained after optimization (our work) and those by X-ray diffraction on the single crystal [4] are summarized in Table 1.

The analysis of table 1 shows that there is short difference between the bond lengths and bond angles obtained by the method theoretically and experimentally [4]. The slight difference may be due to the stability of the molecules, in the case of the crystal by the presence of intra-and intermolecular hydrogen bonds. The fundamental characteristic of the molecular structure is not different for the expected structures. The two benzene rings are coplanar with the C_1-N_1 and $\text{C}'_1-\text{N}'_1$ bonds. These may be due to the stabilization of DBH(OH) by the intramolecular hydrogen bond $\text{OH} \cdots \text{N}$.

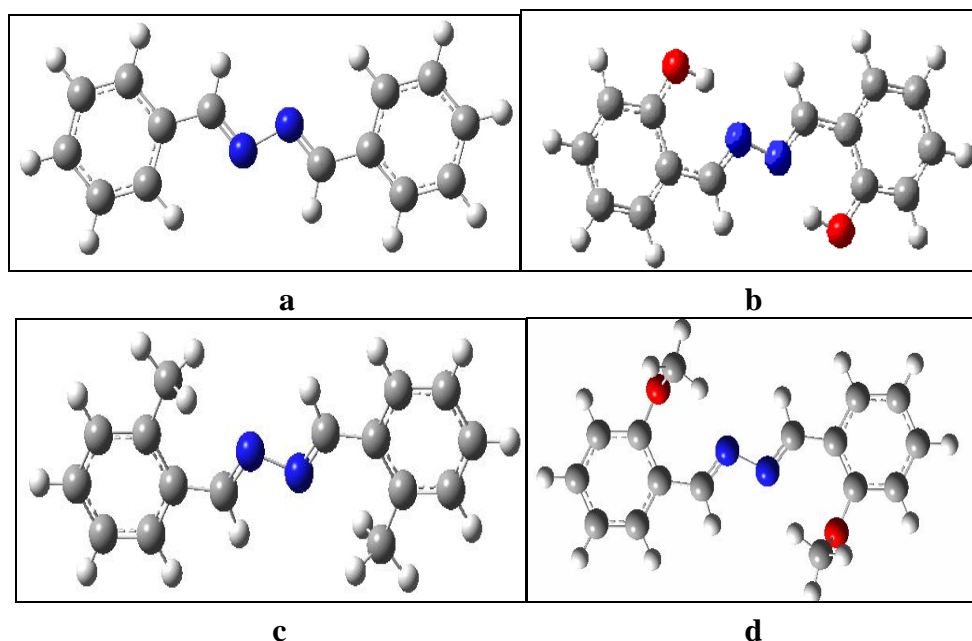


Figure 2: The stable conformations of molecules DBH (R): a) R = H, b) R = OH, c) R = Me and d) R = OMe.

Table 1: Parameters of the bond lengths (Å) and angles torsion (°), fully optimized geometric B3LYP/6-31G (d) and by X-ray diffraction on single crystal.

Parameters	DBH(H)	DBH(Me)	DBH(OMe)	DBH(OH)	DBH(OH)*
N ₁ -C ₁ (Å)	1.288(4)	1.290(2)	1.290	1.297(3)	1.284(2)
N ₁ -N' ₁ (Å)	1.394(7)	1.400(2)	1.402(2)	1.381(7)	1.404(2)
C ₁ -C ₂ (Å)	1.462	1.461(9)	1.460(4)	1.446	1.454(2)
C ₇ -O ₇ (Å)			1.353(9)	1.343(9)	1.350(2)
N ₁ -C ₁ -C ₂ (°)	122.27(8)	125.33	126.08(4)	122.33(5)	121.40(1)
N ₁ -C ₁ -H ₁ (°)	119.97(7)	118.70(4)	118.66(1)	119.58(9)	119.30
C ₁ -N ₁ -N' ₁ (°)	112.07(3)	111.47	110.71(8)	114.30	113.51(1)
C ₂ -C ₁ -H ₁ (°)	117.74(5)	115.96(5)	115.25(3)	118.07(4)	119.3
C ₃ -C ₂ -C ₁ (°)	121.78(6)	115.55(5)	116.59(3)	119.28(1)	120.05(11)
C ₇ -C ₂ -C ₁ (°)	119.20(2)	125.29	125.59(9)	121.96(1)	121.59(11)

*: Crystal [4].

3.2. Relative energy compounds DBH(R)

Figure 3 shows the variation of the relative energy of the compounds DBH(R) with R = H, Me, OH and OMe depending on the twist angle $-\text{C}=\text{N}-\text{N}=\text{C}-$. It is observed that $\theta = 0^\circ$, DBH(OH) with the lowest relative energy is the most stable compound and DBH(OMe) having the greatest relative energy is less stable, while the compounds DBH(Me) and DBH(H) possess intermediate energy. This stability may be due to the presence respectively of the intramolecular hydrogen bond and the gene strique caused by hydroxy and methoxy.

For all compounds of DBH(R), the anti-conformation corresponding to the angle torsion about 180° twist is the most stable. Table 2 records the relative energy for each conformation anti-plane.

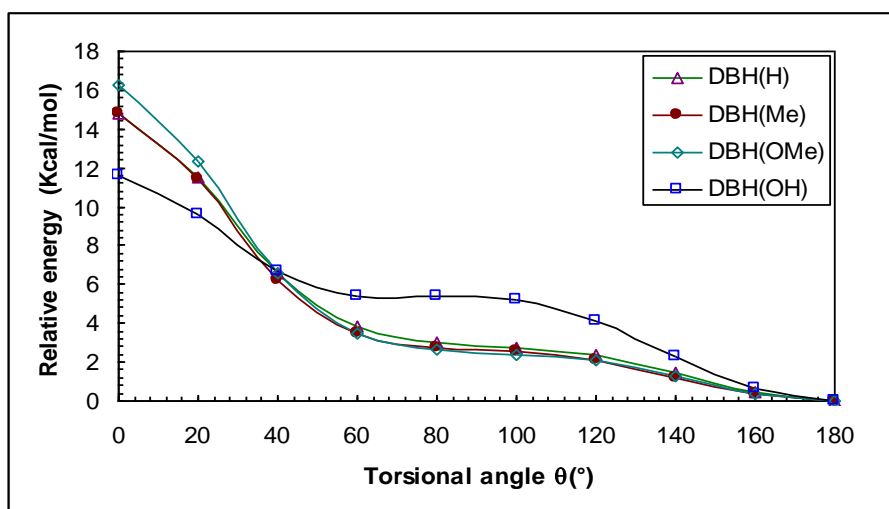


Figure 3: Variation of the relative energy of the compounds DBH (R) (R = H, Me, OH and OMe) as a function of the angle of torsion by the method B3LYP/6-31G (d).

Table 2: Energy (eV/ mol) of compounds DBH(R) for $\theta = 0, 40$ and 180° .

DBH(R)	Relative energy (eV)		
	$\theta = 0^\circ$.	$\theta = 40^\circ$.	$\theta = 180^\circ$.
R = OMe	0.7049	0.2857	-2.7212E-07
R = H	0.6403	0.2843	0
R = Me	0.6417	0.2707	2.7212E-07
R = OH	0.5051	0.2901	-0.0008

4. Inhibitory properties and optoelectronic devices

During the study inhibitory properties, we are interested in the energies of the frontier orbitals HOMO and LUMO. They can be used to predict the adsorption centers for inhibitory molecules. When electrons are transferred, the adsorption is carried out on the soft part of the molecule having the greatest σ (softness) value. This factor defines a local property.

According to Koopman's theorem [9], the energies of the HOMO and the LUMO orbital of the inhibitor molecule are related to the ionization potential (I) and the electron affinity (A) respectively by the following relations: $I = -E_{\text{HOMO}}$ and $A = -E_{\text{LUMO}}$. Absolute electronegativity (χ) and Absolute hardness (η) of inhibitor molecule are given by Pearson [10]. $\chi = \frac{I+A}{2}$ and $\eta = \frac{I-A}{2}$. Softness is the inverse of hardness : $\sigma = \frac{1}{\eta}$. The obtained values

of χ and η are used to calculate the fraction of the electrons transferred (ΔN) from the inhibitor to metallic surface as follow $\Delta N = \frac{\chi_M - \chi_{Inb}}{2(\eta_M + \eta_{Inb})}$ [11].

Using the theoretical value of $\chi_{Cu} = 4.48 \text{ eV/mol}$ and value of $\eta_{Cu} = 0 \text{ eV/mol}$ for copper according to Pearson's electronegativity scale assuming that for a metallic bulk $I = A$, because they are softer than neutral metallic atoms [10]. The fraction of the electrons transferred (ΔN) from the inhibitor to metallic surface of copper (Cu) is calculated for the DBH(R)) in table 3.

Table 3: The calculated quantum chemical parameters of the studied compounds (DBH(R)) (R = H, Me, OH and OMe).

Quantum parameters	DBH(H)	DBH(Me)	DBH(OMe)	DBH(OH)
E_{HOMO} (eV)	-5.9272	-5.8785	-5.4118	-5.8045
E_{LUMO} (eV)	-1.8520	-1.7791	-1.4814	-2.1396
E_{gap} (eV)	4.0752	4.09943	3.9304	3.6648
μ (Debye)	0.0001	0.0003	0.0008	0.000
$I = -E_{HOMO}$ (eV)	5.9272	5.8785	5.4118	5.8045
$A = -E_{LUMO}$ (eV)	1.8520	1.7791	1.4814	2.1396
$\chi = \frac{I+A}{2}$ (eV)	3.8896	3.8288	3.4466	3.9720
$\eta = \frac{I-A}{2}$ (eV)	2.0376	2.0497	1.9652	1.8324
$\sigma = \frac{1}{\eta}$	0.4908	0.4879	0.5089	0.5457
$\Delta N = \frac{\chi_{Cu} - \chi_{Inb}}{2(\eta_{Cu} + \eta_{Inb})}$	0.6015	0.6674	1.01542	0.4654

Since these compounds are inhibitors, we checked the values of their dipole moments which are a measure of the polarity of the polar covalent bands. It is defined as the product of the charges on the atoms and the distance between the two bonded atoms. The total dipole moment, however, reflects only the global polarity of a molecule. For a complete molecule the total molecular dipole moment may be approximated as the vector sum of individual bond dipole moments.

From the data in table 3, energy of highest occupied molecular orbital (E_{HOMO}), energy of lowest unoccupied molecular orbital (E_{LUMO}), energy gap (E_{gap}), dipole moment (μ), electronegativity (χ), electron affinity (A), global hardness (η), softness (σ), ionization potential (I) and the fraction of electrons transferred from inhibitor to copper surface (ΔN), we could consider that the order of increasing efficiency inhibitory molecules (DBH(R)) is as follows: R = OH, H, Me, OMe. This is explained by the following results:

Table 4: Wave absorption, activation energies, Oscillator strength and transitions between orbital HOMO (H) and LUMO (L) of compounds (DBH (R)) (R = H, Me, OH and OMe).

DBH(R)	λ (nm)	E(ev)	Oscillator Strength	Contribution	
R= OMe	$\lambda_1 = 329.99$	3.7572	1.0529	H-1 -> L+1	(0.2129)
				H -> L	(0.6486)
	$\lambda_2 = 297.62$	4.1659	0.0000	H-3 -> L	(-0.1021)
				H-3 -> L+2	(0.1933)
				H-2 -> L+1	(0.3025)
				H-1 -> L	(0.4351)
				H-1 -> L+2	(0.1085)
				H-1 -> L+4	(-0.1028)
				H -> L+1	(0.2366)
				H -> L+3	(0.2621)
	$\lambda_3 = 290.45$	4.2687	0.0939	H3 -> L+1	(0.1872)
				H-3 -> L+3	(-0.1991)
				H-2 -> L	(0.3976)
				H-2 -> L+4	(-0.1118)
				H-1 -> L+1	(-0.2566)
				H-1 -> L+3	(-0.1771)
				H -> L	(0.1228)
				H -> L+2	(-0.3509)
R= H	$\lambda_1 = 304.46$	4.0722	1.2551	H-1 -> L+1	(0.2081)
				H -> L	(0.6584)
	$\lambda_2 = 282.24$	4.3928	0.0178	H-6 -> L+1	(0.2709)
				H-6 -> L+5	(0.1045)
				H-4 -> L	(0.1045)
				H-4 -> L+4	(0.2765)
	$\lambda_3 = 279.12$	4.4420	0.0000	H-3 -> L	(0.3714)
				H-3 -> L+4	(-0.1288)
				H-3 -> L+4	(-0.1161)
				H-2 -> L+1	(0.3345)
				H-1 -> L	(0.3345)
				H-1 -> L+2	(0.2769)
				H -> L+3	(-0.3456)
R = Me	$\lambda_1 = 319.64$	3.8788	1.2292	H-3 -> L+1	(-0.1301)
				H-1 -> L+1	(-0.1301)
				H -> L	(0.6607)
	$\lambda_2 = 304.98$	4.0653	0.0170	H-6 -> L+1	(0.1054)
				H-6 -> L+6	(0.1040)

R = OH	$\lambda_3 = 288.33$	4.3001	0.000	H-4 -> L	(0.6208)
				H-4 -> L+4	(0.6208)
				H-3 -> L	(0.1232)
				H-3 -> L+2	(-0.2227)
				H-2 -> L+1	(0.3377)
				H-1 -> L	(0.4129)
				H-1 -> L+1	(0.4129)
				H-1 -> L+4	(-0.1182)
				HO -> L+1	(-0.1182)
				H -> L+3	(0.3054)
	$\lambda_1 = 352.78$	3.5145	0.9375	H-1 -> L+1	(0.2038)
				H -> L	(0.6548)
	$\lambda_2 = 328.45$	3.7748	0.0123	H-6 -> L+1	(0.1119)
				H-4 -> L	(0.6359)
				H-4 -> L+4	(0.2368)
	$\lambda_3 = 308.91$	4.0136	0.0000	H-3 -> L+2	(-0.1609)
				H-2 -> L+1	(-0.2641)
				H-1 -> L	(0.4976)
				H -> L+4	(-0.1026)
				H -> L+1	(-0.1026)
				H -> L+3	(0.1725)

- Increasing values of dipole moments. This is in agreement with studies by A. Zarrouk et al. quinoxalines on molecules [12].

- The order of the HOMO orbital energies of molecules and the fraction of electrons transferred from inhibitor to copper surface (ΔN) [13].

To interpret the optoelectronic properties of these compounds we calculated the energy gap (Egap is the energy difference between the LUMO and HOMO orbital). Egap is a physicochemical parameter that allows the study of optoelectronic properties and conductive compounds (DBH (R)). This parameter depends on several factors including: the structural parameters, the conformation and substitution on the aromatic rings [14].

Then we determined the values of the absorption maxima with the parameters that are associated with the semi-empirical method ZINDO [8] starting from structures fully optimized by B3LYP/6-31G (d). All these values are reported in table 4.

Note that the value of the theoretical maximum absorption of the compound DBH(H) ($\lambda_{\max} = 304$ nm) is comparable to the experimental benzalazine UV spectrum ($\lambda_{\max} = 300$ nm) [15].

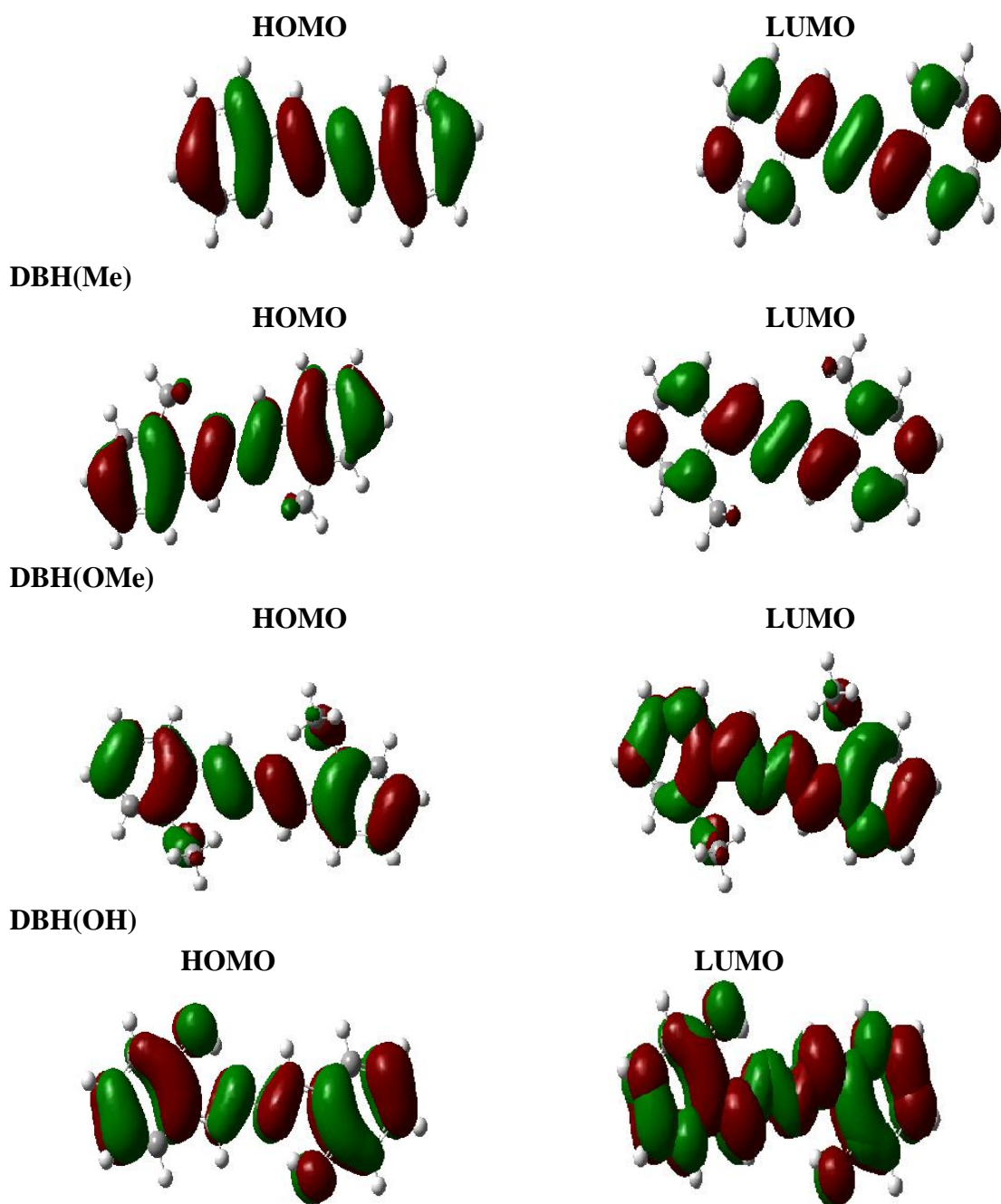


Figure 5: Distribution of electronic frontier orbitals HOMO and LUMO of compounds (DBH(R)) (R = H, Me, OH and OMe).

The results displayed in Table 4 show that molecules with electron-rich groups with low energies Gap have important values of maximum absorption. These values are respectively DBH (OH) (352.75 nm), DBH(OMe) (329.99 nm), DBH(H) (304.46 nm) and DBH(Me) (319.64 nm).

We have represented in Figure 4 the variation of the length of the inter-bond ring ($d_{N-N}(\text{\AA})$) as a function of the torsion angle for all compounds studied.

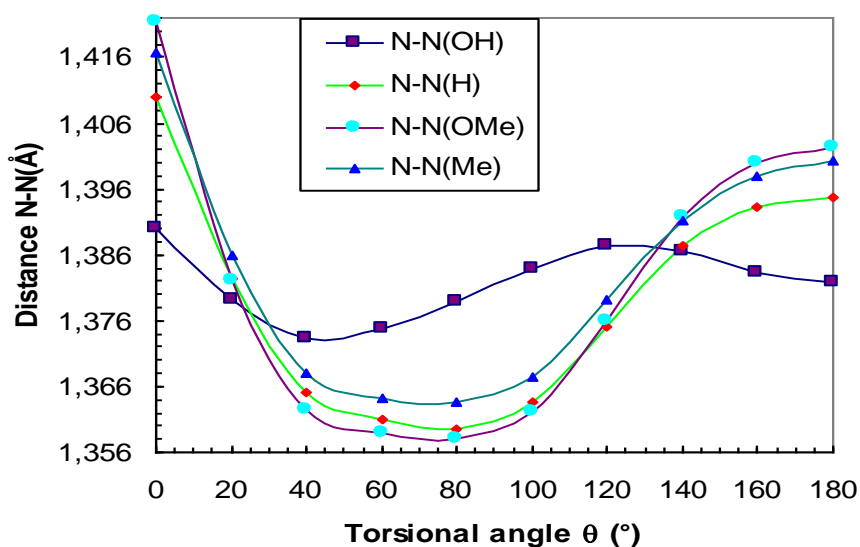


Figure 4: Variation of the distance (d_{N-N} (Å)) as a function of the twist angle θ °.

The analysis of this figure shows that the values of the distance N-N between the two benzyl groups are in the same order for conformations corresponding to $\theta^\circ = 0$ and 180° .

It was found that the inclusion of electron donors were substituted either by inductive or mesomeric effect which increases the distance N-N. The same observation was noted during the study Azines by Kleinpeter [16]. An exception was observed for the compound DBH (OH) which is manifested by the smallest distance d_{N-N} . This can be explained by the presence of strong interactions due to the intramolecular hydrogen bond.

Figure 5 shows the densities of the frontier orbital HOMO and LUMO of various compounds studied (DBH (R)) (R = H, Me, OH and OMe).

We found that this density is delocalized over the entire skeleton. In the case of orbital HOMO, π -bonding character and π -antibonding, respectively, were observed in different units (aromatic rings and the bridge) constituting the molecule studied and between two consecutive units. A reverse phenomenon is observed for the LUMO orbital

5. Conclusion

In this study, we carried out a theoretical study of N, N'-di (ortho-substituted benzyl) hydrazine (DBH (R)) with R = H, Me, OH and OMe with Theory Density Functional (DFT) using the hybrid method B3LYP with the basis 6-31G (d) and the semi-empirical method ZINDO.

The values of bond lengths and bond angles between atoms obtained are comparable to those obtained from the single crystal [4].

The variation of the relative energy in function of the angle of torsion θ -C=N-N=C- shows that the stability of these compounds is due to the presence of the intramolecular hydrogen bond and the gene strique of substituents (R) and the atoms of the bridge.

Molecules having substituents (R)-rich electrons have low energies and important Gap values of the absorption maximum.

It was found that the inclusion of electron donors have been substituted either by inductive or mesomeric effect increasing the distance N-N.

Increasing values of the dipole moments are in agreement with the ΔN results found in the calculation of fractional electron transferred inhibitor molecules to the surface of the metal centers.

References

1. Methods for the Determination of Hazardous Substances, Health and Safety Executive, Suffolk, UK. MDHS Method N° 86 August (1997).
2. INERIS, Emissions accidentelles de substances chimiques dangereuses dans l'atmosphère, Hydrazine, 1-2 (2003).
3. P. Ortega-Barrales A. Molina-Díaz M.I. Pascual-Reguera L.F. Capitán-Vallvey, Solid-phase spectrophotometric determination of trace amounts of hydrazine at sub-ng ml⁻¹ level, *Analytica Chimica Acta* 353 (1997) 115-122.
4. Mijanuddin M., Sheldrick W. S., Mayer-Figge H., Ali M., Chattopadhyay N., *Journal of Molecular Structure* 693 (2004) 161.
5. Grozema F. C., Candeias L. P., Swart M., Van Dujnen P., Wildemen J., Hadzianon G., *J. Chem. Phys.*, 117, 24, (2002) 11366 ; Briere J-F. and Cote M.. *J. Phys. Chem. B.* 108, 10, (2004) 3123; Yungiao Ding. Dacheng Feng, Shengyu Feng, Jie Zhang and Ju Xie, *Polymer*, 47 (2006) 368 ; Katoro Honda, Yukio Furukawa and Furukawa and Hiroyuki Nishide, *Vibrational Spectroscopy*, 40 (2006) 149 ; Bouzakraoui S., Bouzine S. M., Bouachrine M., Hamidi M., *J. Mol. Struct. (THEOCHEM)*, 725 (2005) 39; Bouzine S. M, Bouzakraoui S., Bouachrine M., Hamidi M., *J. Mol. Struct. (THEOCHEM)*, 726 (2005) 26.
6. Lee C., Yang W., R. G., Parr, *Phys. Rev.*, B37, (1993) 161-785.
7. Frisch M. J., Trucks G. W., Schlegel H. B., Scuseria G. E. Robb M. A., Cheeseman J. R., Montgomery J. A., Vreven Jr. T., Kudin K. N., Burant J. C, Millam J. M., Iyengar S. S., Tomasi J., Barone, V., Mennucci B., Cossi M, Scalmani G., Rega N., Petersson G. A., Nakatsuji H., Hada M., Ehara M., Toyota K., Fukuda R., Hasegawa J., Ishida M., Nakajima T., Honda Y., Kitao O., Nakai H., Klene M., Li. X., Knox J. E., Hratchian H. P., Cross J. B., Adamo C., Jaramillo J., Gomperts R., Stratmann R E., Yazyev O., Austin A. J., Cammi R, Pomelli. C., Ochterski J. W., C., Ayala P. Y., Morokuma K., Voth G. A., Salvador P., Dannenberg J. J., Zakrzewski V. G., Dapprich S., Daniels A. D., Strain M. C., Farkas O., Malick D. K., Rabuck A. D., Raghavachari K., Foresman J. B., Ortiz J. V., Cui Q., Baboul A. G., Clifford S., Cioslowski J., Stefanov B. B., Liu G., Liashenko, A., Piskorz, P., Komaromi, I., Martin R. L., Fox D. J., Keith T., Al-Laham M. A., Peng C. Y., Nanayakkara A., Challacombe M., Gill P. M. W., Johnson B., Chen W., Wong M. W., Gonzalez C., Pople J. A., 2003, Gaussian, Inc., Pittsburgh PA, Frisch M. J., Trucks G. W., Schlegel H. B., Scuseria G. E., Robb M. A., Cheeseman J. R., Montgomery J. A., Vreven Jr. T., Kudin K. N., Burant J. C., Millam J. M., Iyengar S. S., Tomasi J., Barone V., Mennucci B., Cossi M., Scalmani

- G., Rega N., Petersson G. A., Nakatsuji H., Hada M., Ehara M., Toyota K., Fukuda R., Hasegawa J., Ishida M., Nakajima T., Honda O., Kitao H., Nakai M., Klene X. Li, Knox J. E., Hratchian H. P, Cross J. B., Adamo C., Jaramillo Y., Gomperts J., Stratmann R., Yazyev R. E., Austin O., Cammi A. J., Pomelli R., Ochterski C., Ayala J. W., Morokuma P. Y., Voth K., Salvador G. A., Dannenberg P., Zakrzewski J. J., Dapprich V. G., Daniels S., Strain A. D., Farkas M. C., Malick O., Rabuck D. K., Raghavachari A. D., Foresman K., Ortiz J. B., Cui J. V., Baboul Q., Clifford A. G., Cioslowski S., Stefanov J., Liu B. B., Liashenko G., Piskorz A., Komaromi P., Martin I., Fox R. L., Keith D. J., Al-Laham T., Peng M. A., Nanayakkara C. Y., Challacombe A., Gill M., Johnson P. M. W., Chen B., Wong W., Gonzalez M. W., Pople C., Gaussian, Inc., Pittsburgh PA, 2003.
8. Bacon A. D., Zerner M. C., *Theo. Chim. Acta* 53 (1979) 21, Anderson W. P., Edwards W. D., Zerner M. C., *Inorganic Chem.* 25 (1986) 2728, Zerner M. C., Lowe G. H., Kirchner R. F., Mueller-Westerhoff U. T., *J. Am. Chem. Soc.* 102 (1980) 589, Ridley J. E., Zerner M. C., *Theo. Chim. Acta* 32 (1973) 111. Ridley J. E., Zerner M. C., *Theo. Chim. Acta* 42 (1976) 223, Thompson M. A., Zerner M. C., *J. Am. Chem. Soc.* 113 (1991) 8210, Zerner M. C., in *Rev. Comp. Chem.*, Lipkowitz Ed. K. B., Boyd D. B, Vol. 2 (VCH Publishing, New York,) (1991) 313-366, Zerner M. C., Correa de Mello P., Hehenberger M, *Int. J. Quant. Chem.* 21 (1982) 251. Hanson L. K., Fajer J., Thompson M. A., Zerner M. C., *J. Am. Chem. Soc.* 109 (1987) 4728.
9. Sastri V. S., Perumareddi J. R., *Corrosion* 53 (1996) 671.
10. Pearson R. G., Absolute electronegativity and hardness: application to inorganic chemistry. *Inorganic chemistry. Inorg. Chem.* 27 (1988) 734.
11. Martinez S., Inhibitory mechanism of mimosa tannin using molecular modeling and substitutional adsorption isotherms. *Mater. Chem. Phys.* 77 (2002) 97.
12. Zarrouk A., Hammouti B., Dafali A., Bouachrine M., Zarrok H., Boukhris S., Al – Deyab S. S., *Journal of Saudi Chemical Society* (2011), doi:10.1016/j.jscs.2011.09.011.
13. Lukovits I., Kalman E., Zucchi F. Corrosion inhibitors-correlation between electronic structure and efficiency. *Corrosion*, 57 (2001) 3.
14. Ferza L., Zgou H., Bouachrine M., Hamidi M., *Chem. News* 26 (2005) 124-130.
15. U.S Departement of Labors, Hydrazine, (2007), <http://www.osha.gov>
16. Kleinpeter E., Stamboliyska B. A., *Tetrahedron* 65, 45 (2009) 9211-9217.