

Structural and Molecular Orbital Properties of Some Boroxine Derivatives-A Theoretical Study

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In the present study, firstly, the variations of the geometric parameters induced by different substituents on boroxine skeleton (symmetrically H, CH₃, Cl, F, NO₂ substituted boroxines) are investigated by using B3LYP/6-31G(d,p), RHF/6-31G(d,p), and MP2/6-31G(d,p) levels of the theory. The second objective is to estimate the substituent effect on the molecular aromaticity of boroxine derivatives using energetic and NICS criteria. Moreover, the effects of different theoretical levels on NICS values have been investigated in a systematic approach. Lastly, a rotational analysis has been performed to investigate the effect of rotation around the B-Me and B-NO₂ bonds on total energy of the system. It has been found that electron withdrawing substituents contribute the aromaticity of boroxine affirmatively. Conversely, electron donors make the system less aromatic. Also, the theoretical vibrational spectra for these boroxine derivatives are presented and compared with the experimental data from the literature.

Key Words: Boroxine, NICS, Aromaticity, DFT, *ab initio*

Introduction

Inorganic cyclic ring systems that are isoelectronic with benzene have been known for many years, of which borazine and boroxine (boroxole) are referred to as "inorganic benzene".¹⁻³ Boroxines are the dehydration products of organo-boronic acids and they have found commercial use in such diverse areas as flame retardant materials,⁴ dopants that enhance lithium ion transference in polymer electrolytes⁵⁻⁷ and recently as boronic acid alternatives in Suzuki-Miyaura coupling reactions.⁸ Alcaraz *et al.* have also investigated boroxine-based compounds as nonlinear optical materials.⁹ It is well-known that boroxines form isolable adducts with many nitrogen donor compounds including amines,¹⁰⁻¹⁴ pyridines,¹⁵ hydrazines,¹⁵ azaindoles,¹⁷ and even salen type ligands.¹⁸

In 1958, Snyder *et al.* reported the synthesis of a 1:1 complex between triphenylboroxine and pyridine, (PhBO)₃·pyridine, and proposed that the coordination of the pyridine occurs at one boron atom within the B₃O₃ ring.¹⁵ On the other hand, 1:1 triorganoboroxine-amine complexes are so stable and easily formed that a convenient literature preparation of (MeBO)₃ from B(OMe)₃ involves the initial formation of (MeBO)₃·pyridine complex followed by removal of pyridine.¹⁹ The chemistry of triorganoboroxines is dominated by ring-cleavage reactions.²⁰

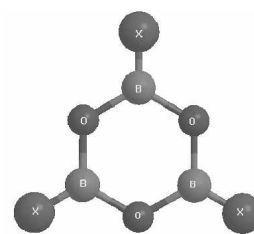
Apart from the synthetic approaches to the boroxine derivatives, there have been many theoretical studies on boroxine and its derivatives. Among them: Beckmann *et al.*, investigated ring strain in boroxine rings,²¹ Doerksen and Thakkar computed the bond orders, quadrupole and octopole moments of some heterocyclic molecules, including boroxine,^{22,23} ring currents and aromaticity of monocyclic systems have been studied by Fowler and Steiner,²⁴ and Tossell investigated the structure, polarizability and vibrational spectra of boroxine.²⁵

It has been proposed that replacing hydrogen atoms of boron in borazine with more electronegative substituents, for example fluorines, will draw more electrons from nitrogen to

boron, thereby enhancing the aromaticity of the molecule.²⁶ Parker *et al.*²⁷ calculated the aromaticity of a series of fluoro derivatives of borazine by carrying out vibrational analysis, and concluded that fluorination on boron increases molecular aromaticity, while fluorination on nitrogen decreases it.

In the last two decades the extent of B-O π bonding in boroxines was the topic of several articles.^{28,29} In 1999, Beckett *et al.*²⁹ estimated the Lewis acidity of boron centers in boroxines in comparison to that of the related borazenes. Generally the boron atoms in boroxines possess a higher Lewis acidity than those in borazenes and therefore, the related boroxines show a much lower aromatic character. Nevertheless, X-ray structure analysis of boroxines gives evidence for the existence of a π-ring system.³⁰

In the present study, we performed theoretical analysis to study the structural and molecular orbital properties as well as the aromaticity of some boroxine derivatives (B₃O₃X₃, X: H, CH₃, Cl, F, NO₂). The aromaticity of the present systems have been investigated by the application of Nucleus Independent Chemical Shifts (NICS).



Method of Calculation

The initial geometry optimizations of all the structures leading to energy minima were achieved by using MM2 method followed by semi-empirical PM3 self-consistent fields molecular orbital (SCF MO) method^{31,32} at the restricted level.³³ Then, geometry optimizations were achieved within the frame-

work of *ab initio* Hartree-Fock (RHF), MP2 calculations and density functional theory (DFT, B3LYP)^{34,35} at the level of 6-31G(d,p) (restricted closed-shell).³² The exchange term of B3LYP consists of hybrid Hartree-Fock and local spin density (LSD) exchange functions with Becke's gradient correlation to LSD exchange.³⁶ The correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional³⁷ and Lee, Yang, Parr (LYP) correlation correction functional.³⁸ The BLYP method gives a better improvement over the SCF-HF results. Its predictions are in qualitative agreement with experiment.³⁹⁻⁴¹ The normal mode analysis for each structure resulted in no imaginary frequencies for all the three methods of calculations.

Absolute NMR shielding values⁴² were calculated using the Gauge-Independent Atomic Orbital method⁴³ with the restricted closed shell formalism employing 6-31G (d,p), 6-311G (d,p), 6-31++G (d,p), 6-311++G (d,p), and cc-pVDZ basis sets⁴⁴ over B3LYP/6-31G (d,p), HF/6-31G (d,p), and MP2/6-31G (d,p) optimized geometries. NICS values were obtained by calculating absolute NMR shielding at the ring centers, NICS (0).

To investigate the effect of rotation around the B-Me and B-NO₂ on the stability of the system, a rotational analysis has been performed at B3LYP/6-31G(d,p) level.

The geometry optimizations and NICS calculations of the present systems have been performed by the use of Gaussian 98 package program.⁴⁵

Results and Discussion

In the present work, the structural and molecular orbital properties of some boroxine derivatives (B₃O₃X₃, X: H, CH₃, Cl, F, NO₂) have been investigated theoretically by the application of B3LYP/6-31G (d,p), RHF/6-31G (d,p), and MP2/6-31G (d,p) type quantum chemical calculations. The effects of substituents (X) present and the basis sets used on the aromaticity of the present systems have also been investigated using NICS calculations. Additionally, the theoretical vibrational spectra have been obtained for these derivatives.

The Geometries. The electronic configuration for boron and oxygen elements are 1s²2s²2p¹ and 1s²2s²2p⁴, respectively. The single bond radius of boron is 0.81 Å, whereas the double bond radius is 0.71 Å. For oxygen atom these values are 0.74 Å and 0.62 Å,⁴⁶ respectively. Hence, B-O single bond length should be 1.55 Å whereas B-O double bond should be 1.33 Å. Table 1 shows various structural properties of the compounds

studied. The DFT calculations yield the order of B-O bond lengths as Cl < H < NO₂ < F < CH₃. Whereas the order is NO₂ < Cl < F < H < CH₃ for the *ab initio* and CH₃ < F < Cl < H < NO₂ for MP2 calculations. Although, the bond length orders are quite different from each other, the presently calculated B-O bond lengths vary between 1.35 Å to 1.41 Å (see Table 1) which show some double bond character as compared to 1.55 Å for the B-O single and 1.33 Å for the B-O double bond lengths in typical respective boron compounds.

The B3LYP geometry optimized structures of the present systems can be seen in Figure 1. The O-B-O and B-O-B bond angles are the same in all the cases (note that all the bond angles in benzene molecule are 120°, indicating a perfect hexagon and aromaticity). The degree of aromaticity in monocyclic hetero-aromatic compounds can be judged by comparing certain structural (e.g.: angles) data with benzene. Some struc-

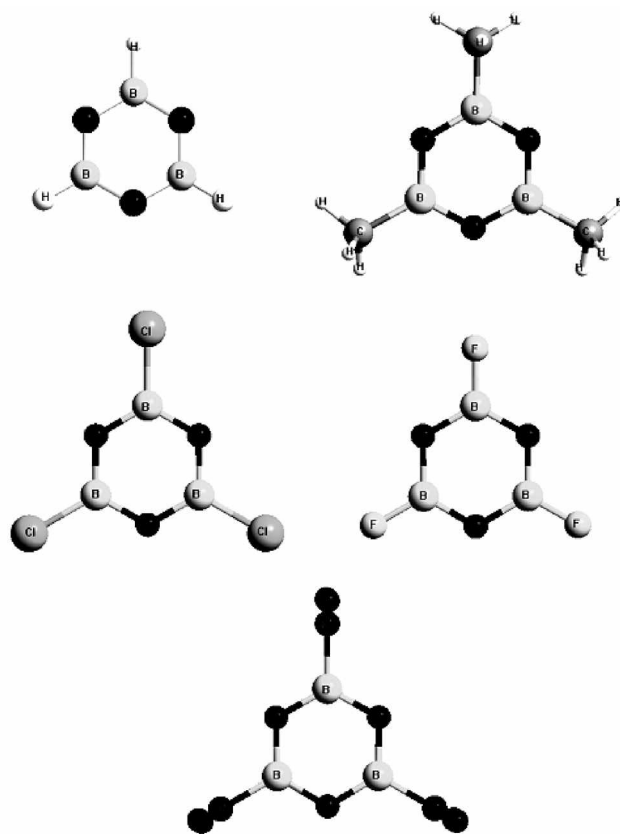


Figure 1. The geometry optimized structures of the present systems (B3LYP).

Table 1. Some structural data for the present systems (bond lengths are in Å, and angles in degrees, basis set: 6-31G (d,p), refer to Scheme 1 for the structures).

X	B3LYP/6-31 G (d,p)				RHF/6-31 G (d,p)				MP2/6-31 G (d,p)				Point group
	B-X	B-O	OBO	BOB	B-X	B-O	OBO	BOB	B-X	B-O	OBO	BOB	
H	1.1825	1.3645	119.0	120.9	1.1825	1.3645	119.0	120.9	1.1805	1.3805	120.3	119.7	C _{3h}
CH ₃	1.5685	1.3835	118.4	121.6	1.5735	1.3705	118.0	122.0	1.4815	1.3335	119.7	120.3	C ₃
Cl	1.7495	1.3585	119.4	120.6	1.7495	1.3585	119.5	120.5	1.7345	1.3775	120.7	119.3	C _s
F	1.3175	1.3745	120.6	119.4	1.3035	1.3595	119.9	120.1	1.3225	1.3765	121.2	118.8	D _{3h}
NO ₂	1.5135	1.3665	121.9	118.0	1.5165	1.3505	121.5	118.5	1.5025	1.4055	119.5	120.5	C ₁

tural data (B-O bond lengths, O-B-O bond angles and symmetry point groups) of the boroxine derivatives are given in Table 1. The bond angles increase toward 120° as the electro-negativity of the substituents increases (from CH_3 to F). This is expected since the electronegative substituent on boron pulls the lone pair electrons of the oxygen toward boron. Therefore, the substituents that strongly withdraw both the σ - and π -electrons, e.g. nitro group, should be expected to attract the lone pairs of oxygens into the boroxine ring and consequently increasing the molecular aromaticity; while those electron-donating substituents, e.g. methyl group, may be expected to cause the contrary variations in the aromaticity.

The 3-D electrostatic potential maps, which represent the charge distribution in the structure, of the presently considered systems are shown in Figure 2. In each case, the areas in black represent negative charge development, however, the lighter areas are positively charged. As can be seen, going from H to NO_2 the electron density on the substituents increase

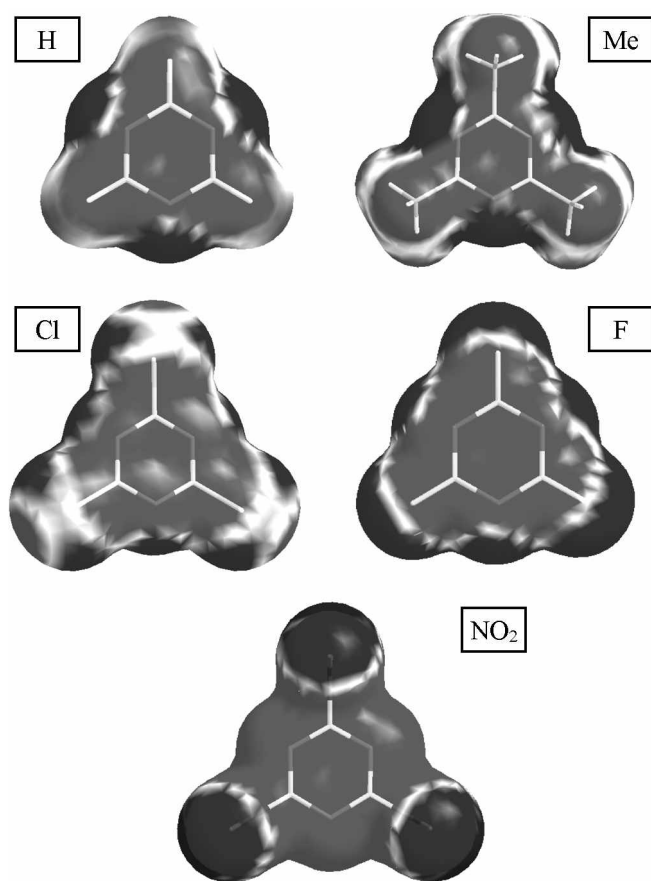


Figure 2. 3-D electrostatic potential maps of the present boroxine derivatives.

however, the electron density on oxygens of the boroxine ring decreases. The electron density of the whole molecule is most uniformly distributed in the case of F substitution. Thus, we expect that F substituted derivative is the most aromatic one among all.

The Stabilities. Energetics: Table 2 gives the total energies (B3LYP/6-31G (d,p), RHF/6-31G (d,p) and MP2/6-31G (d,p)), for the presently considered boroxine derivatives. The structures are found to be stable, and in each case the lowest energy has been obtained with the B3LYP type calculations (except Cl substituted boroxine compound).

NICS: Aromaticity continues to be an actively investigated area of chemistry. The simplest criterion for aromatic compounds is that they possess cyclic conjugated π -systems containing the proper number of π -electrons (i.e., the Hückel rule). While this criterion is robust enough to predict the aromaticity of a host of neutral and charged ring systems, it is not always a clear indicator of aromaticity for more complex systems (as in our case).

Aromaticity is expressed by a combination of properties in cyclic delocalized systems. In general, aromaticity is discussed in terms of energetic, structural and magnetic criteria.⁴⁷⁻⁵² In 1996, Schleyer has introduced a simple and efficient probe for aromaticity: Nucleus-independent chemical shift (NICS),⁵³ which is the computed value of the negative magnetic shielding at some selected point in space, generally, at a ring or cage center. Negative NICS values denote aromaticity (-11.5 for benzene, -11.4 for naphthalene) and positive NICS values denote antiaromaticity (28.8 for cyclobutadiene) while small NICS values indicate non-aromaticity (-2.1 for cyclohexane, -1.1 for adamantane). NICS may be a useful indicator of aromaticity that usually correlates well with the other energetic, structural and magnetic criteria for aromaticity.^{42,54-57} Resonance energies and magnetic susceptibilities are measures of the overall aromaticity of a polycycle, but do not provide information about the individual rings. However, NICS is an effective probe for local aromaticity of individual rings of polycyclic systems.

In the present study, the aromaticity of the boroxine derivatives have been investigated by the application of the NICS calculations. The work has been enlarged with the use of different basis sets since it is reported earlier⁵⁸ that NICS is somewhat dependent on the choice of basis set. The results of our calculations are shown in Table 3. As in the case of borazine, Cl, F, and NO_2 substituted derivatives have been expected to be more aromatic than the H and Me substituted boroxines due to the reason that, the electronegative character of the former substituents force the lone pair electrons of the oxygen toward boron thus, increase the π conjugation in the ring system. The aromaticity of the boroxine ring has been

Table 2. Total energies of the present systems (Energies in Hartrees).

Total Energy	H	CH_3	Cl	F	NO_2
B3LYP/6-31G (d,p)	-302.3218716	-420.3312470	-1677.5594948	-600.2489323	-915.8607249
RHF/6-31G (d,p)	-300.7041996	-417.8750098	-1677.5594946	-597.5022031	-911.1518175
MP2/6-31G (d,p)	-301.4858614	-419.0612797	-1678.7415392	-598.7746064	-912.3578300

Table 3. The NICS (ppm) values of the present systems, obtained with different methods and basis sets (6-31G (d,p) basis set was used for each geometry optimization. Some values are missing due to the computational cost).

System	Geom. Opt. Method	6-31G (d,p)	6-311G (d,p)	6-31++G (d,p)	6-311++G (d,p)	cc-pVDZ
H	B3LYP	-0.4446	-0.8295	-0.4714	-0.4618	-0.2431
	RHF	-0.4424	-0.8722	-0.4961	-0.6393	-0.3413
	MP2	-0.6462	-1.0638	-0.7281	-	-0.5031
CH ₃	B3LYP	-0.4045	-0.6339	-0.3571	-0.4736	-0.2111
	RHF	-0.2732	-0.5593	-0.2781	-0.5317	-0.2608
	MP2	-0.4739	-0.7739	-	-	-
Cl	B3LYP	-1.6697	-1.5036	-1.3743	-1.2367	-1.4639
	RHF	-1.8569	-1.7158	-1.6660	-1.6434	-1.7808
	MP2	-1.9311	-1.8112	-1.7754	-1.7388	-1.8369
F	B3LYP	-3.1484	-3.5613	-2.9283	-3.1868	-3.5316
	RHF	-2.8122	-3.5513	-2.8196	-3.3263	-3.6697
	MP2	-2.9113	-3.6354	-2.9308	-3.4209	-3.6880
NO ₂	B3LYP	-2.2413	-2.5390	-2.1603	-2.2233	-2.5244
	RHF	-2.3521	-2.9169	-2.4358	-2.7162	-3.0139

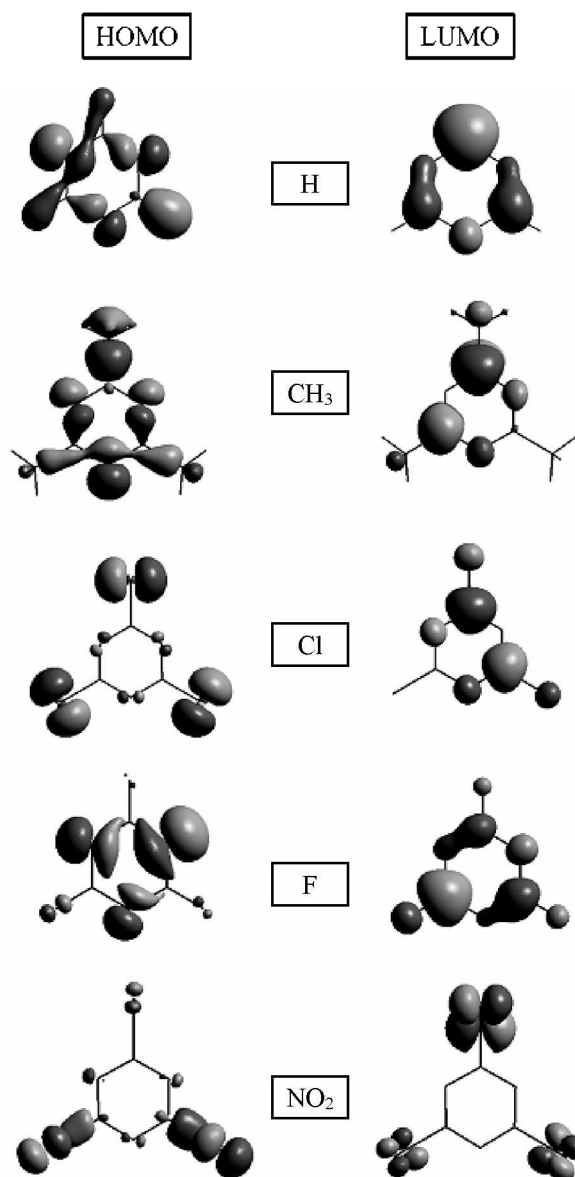
expected to increase with substitution of more electronegative substituents on the boron atom. Therefore, aromaticity and NICS (ppm) values for Cl, F, and NO₂ substituted derivatives must be greater than H and CH₃ derivatives. According to the results in Table 3, the aromaticity of the present structures can be given in the following order: F > NO₂ > Cl > H > CH₃. When the NICS values obtained are compared with benzene (-9.5), and borazine (-1.3), boroxine is the least aromatic among all.

The Frontier Molecular Orbital Energies. The frontier molecular orbital energies (HOMO and LUMO) as well as the interfrontier molecular orbital energy gap values ($\Delta\epsilon = \epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}}$) are shown in Table 4. The frontier molecular orbitals of the present systems can be seen in Figure 3.

As seen in the figure, contributions of each oxygen and boron orbitals to the HOMO of boroxine are quite different and the interaction of orbitals allow some delocalization of the electrons. Such kind of partial delocalization is also valid for the methyl derivative. Whereas, in the rest of the structures, the electrons localized in the HOMO. The chlorine derivative, in that respect deserves to be mentioned because the HOMO is highly symmetrical. When the chlorine and fluorine derivatives are compared for the HOMO, the main contribution in the former case is by chlorine atomic orbitals. Whereas, in the later case, the oxygen atoms are the main contributors. In the case of the LUMOs, mostly boron atoms are the main contributors. However, not in all the cases the borons contribute equally or contribute any. Some of them contribute nil, e.g. the nitro derivative. In the LUMOs mainly the π -type symmetry exists.

Table 4. The frontier molecular orbital energies and the interfrontier molecular orbital energy gaps (B3LYP/6-31G(d,p) level of theory, energies in Hartree).

	H	CH ₃	Cl	F	NO ₂
LUMO	-0.0157	0.0151	-0.0316	0.0116	-0.1182
HOMO	-0.3360	-0.3101	-0.3381	-0.3839	-0.3303
$\Delta\epsilon$	0.3203	0.3252	0.3065	0.3955	0.2121

**Figure 3.** Molecular orbital energy schemes of the present systems.

Vibrational Spectra. The vibrational frequencies of the boroxine derivatives are shown in Table 5 (at the DFT (B3LYP) level of theory using the standard 6-31G (d,p) basis set). The normal mode analysis for each structure yielded no imaginary frequencies for the 3N-6 vibrational degrees of freedom, where N is the number of atoms in the system. This indicates that the structure of each molecule corresponds to at least a local minimum on the potential energy surface.

Normal modes of the same symmetry are always mixed to some extent. However, in all cases it was possible to assign the dominant motion for selected modes.

Some characteristic normal modes for boroxine (H) are 910 cm^{-1} (out of plane B-H bending), 1250 and 1468 cm^{-1} (ring stretchings) and 2766 cm^{-1} (asymmetric B-H stretching). The experimental values for the above frequencies are 918, 1213, 1389 and 2620 cm^{-1} ,⁵⁹ respectively. For the Cl derivative the following normal mode values have been calculated: 181 cm^{-1} (B-Cl wag), 415 cm^{-1} (O-B-O bending), 813 cm^{-1} (B-Cl stretching) and 1289 cm^{-1} (B-O stretching). The calculated frequencies are very close to experimental values, 150 cm^{-1} , 390 cm^{-1} , 755 cm^{-1} and 1345 cm^{-1} ,⁶⁰ respectively. Here are some characteristic frequencies for the F derivative, 370 cm^{-1} (B-F bending, exp: 316 cm^{-1}), 824 cm^{-1} (B-O stretching, exp: 826 cm^{-1}) and 1027 cm^{-1} (B-O stretching, exp: 964 cm^{-1}). Experimental values for F derivative have been taken from Ref 61.

Table 5 presents all of the calculated vibrational frequencies of the systems under present consideration. However, the data presented here would be helpful for further studies on boroxine derivatives. The ring stretching frequencies have been marked with an asterisk (*) in Table 5. The ring stretching frequency is an important factor to determine the change of aromaticity. The symmetric stretching frequency of the boron atoms of the main ring is 1027.7 cm^{-1} , 1289.3 cm^{-1} and 1403.2 cm^{-1} for H, Cl and F derivatives, respectively. The symmetric stretching frequency of the oxygen atoms of the main ring is 824.5 cm^{-1} , 885.2 cm^{-1} and 978.5 cm^{-1} for H, Cl and F derivatives, respectively. These results indicate that the ring stretching frequency increases with the increase in the aromaticity of the system.

Rotational Analysis. A rotational analysis at B3LYP/6-31G (d,p) level has been performed, in order to investigate the effect of conformation of the methyl group in CH_3 and the nitro group in NO_2 , on the total energy of each system. For this purpose, the methyl and nitro groups have been rotated around the B- CH_3 and B- NO_2 bonds from 0° to 120° and from 0° to 180°, respectively, by increasing the angle 10 degrees in each step. The variation of the total energy by rotation can be seen in Figure 4 and Figure 5.

The effect of rotation of the methyl group on methyl substituted boroxine system (CH_3) can be seen in Figure 4. The calculations resulted in a minimum at 90° (with a total energy of -420.3312474 Hartree) and a maximum at 0°. Figure 5 shows the variation of the relative energy of the nitro substituted boroxine derivative (NO_2) with respect to the most stable conformation. Again the minimum has been obtained at 90°. The minimum energy structures obtained by the rotational analysis and geometry optimizations are exactly the same for both cases.

Table 5. Fundamental normal modes of the boroxine derivatives calculated at the DFT (B3LYP) level of theory using the standard 6-31G (d,p) basis set (Frequencies are in cm^{-1} and * indicates the stretchings of the boroxine ring).

	H	CH_3	Cl	F	NO_2
1	161.7	31.6	90.9	125.8	34.9
2	162.8	37.2	113.5	126.1	37.3
3	370.4	40.0	113.5	131.2	38.6
4	*535.4	112.2	181.8	312.2	46.7
5	*535.7	112.9	181.8	312.9	68.4
6	*824.5	115.4	*393.4	*452.8	69.3
7	910.4	226.1	*415.6	*453.0	110.8
8	910.6	226.3	*415.6	547.5	110.9
9	910.8	378.5	439.3	*566.8	163.3
10	1017.6	*449.0	619.4	661.6	163.8
11	1017.7	*449.2	619.4	661.8	188.4
12	*1027.7	486.6	750.7	740.3	273.3
13	1134.5	486.8	*813.0	*814.0	*293.1
14	*1250.2	*531.9	*813.0	*978.2	*338.5
15	1262.6	582.2	*885.2	*978.5	*338.7
16	1262.9	793.5	*1289.3	*1247.7	*616.7
17	*1468.5	793.8	*1289.3	*1403.0	*616.9
18	*1468.8	*807.3	*1302.4	*1403.2	624.6
19	2750.6	905.0	*1311.4	*1482.7	624.8
20	2750.8	905.2	*1481.4	*1483.1	*684.3
21	2766.2	924.9	*1481.4	*1527.7	*684.5
22		925.1			707.4
23		927.5			711.7
24		929.9			*798.4
25		*1168.8			*825.4
26		*1256.2			*895.5
27		*1256.8			*895.8
28		*1258.3			*1254.8
29		1360.0			*1255.2
30		1360.3			*1256.5
31		1395.4			*1258.5
32		*1412.1			*1434.6
33		*1412.4			*1436.0
34		1475.6			1532.3
35		1483.8			1532.8
36		1483.8			1533.4
37		1485.9			1618.4
38		1486.6			1619.1
39		1486.7			1624.2
40		3039.0			
41		3039.0			
42		3039.1			
43		3105.2			
44		3105.2			
45		3105.4			
46		3142.7			
47		3143.1			
48		3143.2			

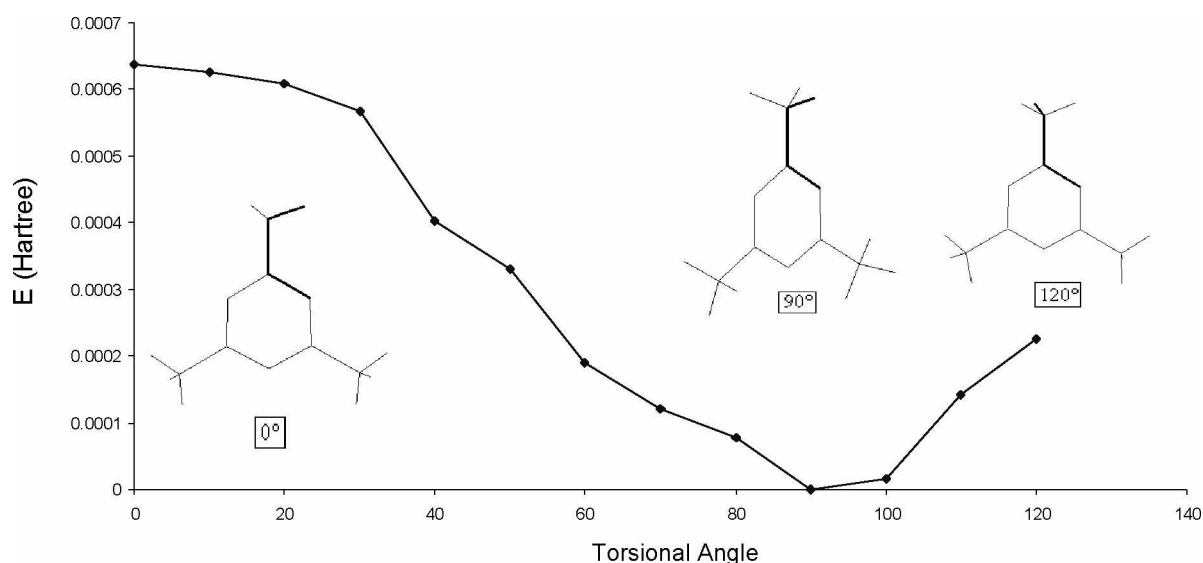


Figure 4. Effect of rotation around the B-CH₃ bond on total energy of the system. Dihedral angle where the rotation takes place is indicated by solid bonds.

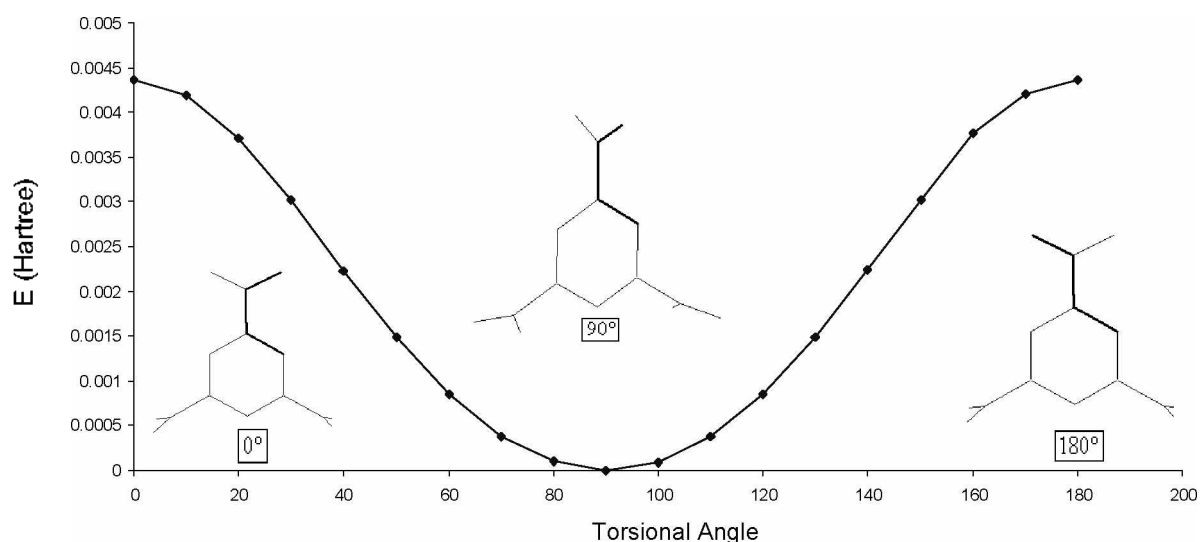


Figure 5. Effect of rotation around the B-NO₂ bond on total energy of the system. Dihedral angle where the rotation takes place is indicated by solid bonds.

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