

Polarizabilities and energetics of boroxopyrrole homologues studied by *ab initio* and density functional methods

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Abstract : Molecular geometries, static polarizabilities and energetics have been calculated for the boroxopyrrole (isoelectronic to pyrrole) homologues including boroxopyrrole ($B_2O_2H_3N$), boroxophosphorylpyrrole ($B_2O_2H_3P$), boroxoarsenylpyrrole ($B_2O_2H_3As$) and boroxoantimonylpyrrole ($B_2O_2H_3Sb$) at the Hartree-Fock by *ab initio* and Density Functional Theory (DFT) by choosing combined exchange correlation potentials B3LYP and B3PW91. All the calculations utilized the 6-311G basis set for lighter atoms and 3-21G for heavier atoms. The influence of substitution with heavy atoms on molecular properties of the homologues was examined theoretically. The calculated results here, show that substitution of the heteroatom with heavy atoms, systematically, increases the individual components of static polarizability, α . This property has been discussed in term of Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) energies. Further, to check the adequacy of the method and the suitability of the basis set, the normal mode frequencies in C_{2v} symmetry was examined theoretically for $B_2O_2H_3N$ and compared with available experimental data.

Keywords : Polarizability, energetics, dipole moment, boroxopyrrole, HOMO-LUMO RHF, DFT.

In the past decade, advancement in computer technology and methodology of molecular orbital (MO) calculation make it possible to calculate response properties due to perturbation in molecular systems within a realistic computation time. Studies on MO calculation of static polarizabilities and hyper polarizabilities have been performed extensively with increasing importance of molecular nonlinear optics for laser wavelength conversion and basic research of optical physics. MO calculation can be a good tool for obtaining some insight into molecular property and as a result, in establishing the structure-property relationship. In the present work, boroxopyrrole ($B_2O_2H_3N$) and its homologues have been studied with regard to possible organic nonlinear optical materials, similar to pyrrole and furan homologues, well known for their optical properties. Our idea of choosing boroxopyrrole goes along the same lines of trichloroboroxine ($B_3O_3Cl_3$) which was first reported in 1951¹ and methods for synthesizing this interesting compound have appeared in the literature¹⁻³. Trichloroboroxine has been investigated for possible in-

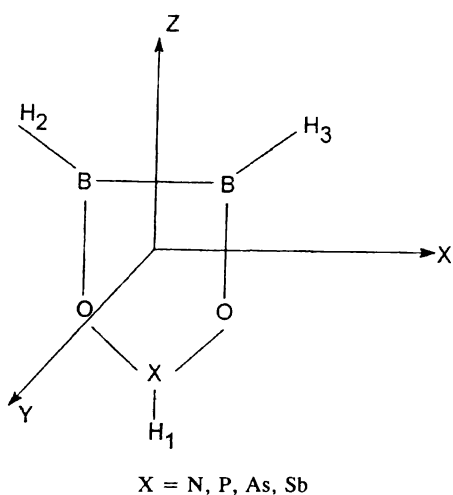
dustrial use as a boronizing agent in steel production⁴. Furthermore, borazines, known as inorganic benzene, is isoelectronic with benzene and its derivatives^{5,6} and has many of its physical properties similar to those of benzene. Hence, it prompted us to investigate the energetics, geometries and static polarizabilities of boroxopyrrole and its homologues by *ab initio* and density functional calculations.

Computational methods :

The various energetics and static polarizabilities alongwith optimized geometries of boroxopyrrole and its homologues were calculated at the Hartree-Fock, DFT (B3LYP)^{7,8} and DFT (B3PW91)⁹ levels of theory using the standard 6-311G basis set. B3LYP is Becke's three parameter hybrid method with LYP correlation functional whereas B3PW91 is Becke's exchange potential clubbed with Perdew-Wang 91 correlation function. The molecular geometries were optimized by keeping root mean square (rms) gradient at 1.0 kcal/Å/mol with Polak-Ribierre gradient method, an algorithm, which is fast and accurate,

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has been employed for all levels of calculations. All the calculations of the structure (figure) were carried out using Hyperchem 7.5 program¹⁰ keeping C_{2v} symmetry of the boroxopyrrole homologues. Since 6-311G basis sets are not defined for As and Sb (heavy atoms) in the software so 321G basis set has been used. The main object of study is, the effect of substitution due to heavy atoms in the ring on physical and optical properties in terms of ionization potential (-HOMO), electron affinity (-LUMO), dipole moment and static polarizability. The theoretical vibrational spectra of boroxopyrrole have also been chalked out in all the three methods, in order to confirm the equilibrium geometry.



Results and discussion

The calculated values, in the present work, are given in Tables 1–8. The equilibrium geometries of the boroxopyrrole and its homologues in three methods are shown in Table 1. By looking at the metrical parameters (Table 1), two important aspects require more attention, first, a regular increase in the bond lengths attached to the hetero atoms and the decrease in the O-X-O angle in all the three methods from N \rightarrow Sb. The X-H bond length increase is also reflected in terms of net atomic charge change on H-atom from positive to negative value (Table 7) shows that the X-H bond changes its acidic property (X = N, P) to basic property (X = As, Sb). The O-atoms attached to heteroatoms show a regular increase in the negative atomic charges. The RHF indicate almost one electron transfer on O-atoms in the molecule but the inclusion of electron correlation B3LYP and B3PW91 modifies the values at 0.75e charge, which seems to be logical, however no experimental data are available for

comparison. The increase in the X-O bond leads to decrease in the O-X-O angle due to the substitution of heteroatom in the homologues, which may be attributed to the charge redistribution in the heavy atom due to availability of d and f orbitals. Second is that pyrrole ring is planar with N-H bond in the plane, whereas, the X-H bond is found to be out of plane (Z-axis) and forms a torsion angle ranging from about 110° to 84° for X = N, P, As, Sb respectively (see Table 1). In addition, the O-X-O plane is observed to be bent with angle ranging from 5° to 8° with respect to O-B-B-O plane from N \rightarrow Sb heteroatoms. The equilibrium geometry of pyrrole is also given as footnote in Table 1. Very recently, Tian¹⁶ working on carboboranes, calculated the B-B distance in the range of 1.748–1.774 Å at B3LYP/6-311G level of theory which compares well with our values in the range of 1.714–1.758 Å (Table 1).

Dipole moment, μ and polarizability, α :

Since, both dipole moment, μ and linear polarizability α , are the most fundamental electric response properties, hence, calculation of these values, provides a good basis for discussing the reliability of the results of the electronic states with various theoretical models^{11,12}. These properties have been discussed for furan and its homologues series with highly sophisticated method^{13,14}. Polarizability is defined as coefficients of the next Taylor expansion of the total electric dipole moment μ_{total} with respect to the applied electric field, F

$$\mu_{\text{total}} = \mu + \alpha F + \beta FF/2 + \gamma FFF/6 + \dots \quad (1)$$

where μ is the permanent electric dipole moment, α is the linear polarizability, β is the first hyperpolarizability and γ is the second hyperpolarizability. The present work reports the linear polarizability and dipole moment values. For the calculation of α , the finite electric field value F was set at 0.005 atomic units. The calculated result of dipole moment and polarizability of the homologues with binding energies are in atomic units given in Tables 2–5. The mean polarizability α_s and anisotropy, $\Delta\alpha$ are defined as :

$$\alpha_s = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3 \quad (2)$$

$$\Delta\alpha = \{[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2]/2\}^{1/2} \quad (3)$$

The results show that the absolute values of the dipole moment increase with the inclusion of the electron correlation of higher levels. This means that the correlation functions become necessary for the charge separation in

Table 1. Theoretical equilibrium geometries for the boroxopyrrole ($B_2O_2H_3X$) homologues (distances in Angstroms and angles in degrees) at 6-311G basis set [$X = N, P, As, Sb$]

System	RHF				DFT							
					B3LYP				B3PW91			
	N	P	As	Sb	N	P	As	Sb	N	P	As	Sb
B-B	1.714	1.746	1.758	1.754	1.694	1.725	1.726	1.738	1.692	1.723	1.732	1.714
B-O	1.371	1.372	1.374	1.374	1.381	1.385	1.383	1.362	1.383	1.384	1.377	1.605
X-O	1.427	1.735	1.809	1.989	1.486	1.8	1.86	2.069	1.471	1.798	1.864	2.038
X-H	1.002	1.434	1.538	1.694	1.031	1.459	1.56	1.727	1.026	1.46	1.554	1.724
B-H	1.179	1.181	1.179	1.171	1.181	1.189	1.19	1.177	1.186	1.191	1.188	1.184
B-O-X	114.4	118.8	118.2	117.7	112.6	115.6	116.3	115.9	112.6	115.6	116.6	115.1
O-X-O	106.2	91.3	89.6	84.3	105.3	92.1	89.3	83.1	105.8	92.2	88.9	84.9
H-X-O	105.3	96.7	98.8	92.8	103.5	95.4	97.5	90.9	103.8	95.4	97.6	91.7
O-X-H-O	112	96.9	98.8	84.4	108.4	92.7	90.3	90.8	110.5	95.6	97.5	85

(Torsion angle)

For arsenic and antimony atoms, 3-21G basis set has been taken.

N-H (0.9860 Å), C-H (1.0654 Å), C-N (1.3719 Å), C-C (1.4284 Å), C=C (1.3615 Å), C-N-C (109.5°).

Table 2. Binding energy, dipole moment and individual components of the polarizability of boroxopyrrole ($B_2O_2H_3N$) calculated with 6-311G basis set

Method	E (+255)	μ_z	α_{xx}	α_{yy}	α_{zz}	α_s	$\Delta\alpha$
RHF	-0.1817	0.6757	41.3719	36.9964	22.2834	33.5506	17.3203
B3LYP	-1.5195	0.5567	49.4824	41.2477	25.2869	38.6723	21.307
B3PW91	-1.5334	0.5622	49.4804	40.7804	25.1986	38.4865	21.3066

1 a.u. = 2.5418 Debye.

Table 3. Binding energy, dipole moment and individual components of the polarizability of boroxophosphopyrrole ($B_2O_2H_3P$) calculated with 6-311G basis set

Method	E (+541)	μ_z	α_{xx}	α_{yy}	α_{zz}	α_s	$\Delta\alpha$
RHF	-0.5726	0.3774	55.086	42.6106	35.6600	44.4523	17.0525
B3LYP	-2.1937	0.5753	67.9966	48.0105	38.5306	51.5126	26.0591
B3PW91	-2.2075	0.5690	67.5298	47.7504	38.2540	51.178	25.8697

Table 4. Binding energy, dipole moment and individual components of the polarizability of boroxoarsenylpyrrole ($B_2O_2H_3As$) calculated with 6-311G/3-21G

Method	E (+2423)	μ_z	α_{xx}	α_{yy}	α_{zz}	α_s	$\Delta\alpha$
RHF	-1.3488	0.5653	60.8199	45.3362	39.5926	48.5829	19.0176
B3LYP	-3.9765	0.8767	70.9811	48.3964	41.7968	53.7247	26.5080
B3PW91	-4.0899	0.8867	71.1285	48.3531	41.7673	53.7497	26.6849

Table 5. Binding energy, dipole moments and individual components of the polarizability of boroxoantimonylpyrrole ($B_2O_2H_3Sb$) calculated with 6-311G/3-21G

Method	E (+6487)	μ_z	α_{xx}	α_{yy}	α_{zz}	α_s	$\Delta\alpha$
RHF	-0.0224	1.1653	60.8409	48.2727	42.7677	50.6271	16.0453
B3LYP	-3.4593	0.8785	72.8364	51.5613	44.8285	56.4087	24.8704
B3PW91	-3.7398	1.0354	70.1158	46.9427	39.291	52.1165	21.4419

a molecule. The components of polarizability, mean polarizability (α_s) and anisotropy ($\Delta\alpha$) show a regular increase as one goes from heteroatom N \rightarrow Sb. The α_{xx} component of boroxopyrrole is smaller than that of the other homologues is because of the larger HOMO-LUMO energy gap (i.e. transition energy) for boroxopyrrole as compared to other homologues (Table 6). The ionization potential (-HOMO) and electron affinity (-LUMO) values are shown in Table 6. HOMO-LUMO energy gap further

confirms the increase in the μ - and α -values. Thus it is found theoretically that the individual components of α of these homologues are increased when heteroatoms are substituted with heavier atoms. The vibrational frequencies for boroxopyrrole ($B_2O_2N_3H$) molecule under three methods, mentioned in the text, are reported in Table 8. The selected normal modes are compared with the available data wherever possible. The comparison of the calculated result authenticates the adequacy and reliability of the various theoretical models.

Table 6. Frontier orbital energies (eV) [HOMO-LUMO] for $B_2O_2H_3X$ homologues at 6-311G basis set [X = N, P, As, Sb]

System	DFT											
	RHF				B3LYP				B3PW91			
	N	P	As	Sb	N	P	As	Sb	N	P	As	Sb
(-HOMO)	11.7844	11.1052	10.6778	10.3517	8.0111	7.6876	7.3411	6.7439	8.0721	7.7032	7.3852	7.2994
(-LUMO)	-1.3824	-1.4919	-1.6356	-1.2710	2.2750	2.2099	2.0138	2.4609	2.3727	2.2440	2.0610	2.1687
ΔE	13.1668	12.5971	12.3134	11.6227	5.7361	5.4777	5.3273	4.2830	5.6994	5.4592	5.2242	5.1307

Ionization potential (-HOMO) of pyrrole is 8.2087 eV at 6-311G basis set (RHF) (present work) identical to 8.208 eV, taken from CRC Hand Book.

Table 7. Net atomic charges on various atoms in boroxopyrrole ($B_2O_2H_3X$) [X = N, P, As, Sb]

System	RHF				B3LYP				B3PW91			
	N	P	As	Sb	N	P	As	Sb	N	P	As	Sb
B	0.350	0.428	0.406	0.400	0.235	0.288	0.266	0.240	0.223	0.278	0.255	0.241
O	-0.570	-0.974	-1.013	-1.029	-0.412	-0.727	-0.769	-0.775	-0.418	-0.731	-0.775	-0.784
N	0.008	1.056	1.267	1.468	-0.058	0.812	1.023	1.172	-0.064	0.793	1.003	1.168
H1	0.351	0.018	-0.060	-0.174	0.336	0.048	-0.027	-0.112	0.348	0.065	-0.007	-0.100
H2	0.044	0.009	0.004	-0.018	0.038	0.008	0.005	0.013	0.053	0.022	0.020	0.009
H3	0.044	0.009	0.004	-0.018	0.038	0.008	0.005	-0.044	0.053	0.022	0.020	0.009

Table 8. Calculated vibrational frequency of boroxopyrrole ($B_2O_2H_3N$) at three levels of theory using the 6-311G basis set

Symmetry	Calculated frequency			Assignment	Experimental frequency ^a
	RHF	B3LYP	B3PW91		
A'	460.7 (32)	463 (32)	465 (30)	O-B-B-O wag	
	634.7 (14)	631 (13)	629 (12)	O-N-O bend	
	781 (43)	789 (45)	790 (40)	H-B-B-H bend	
	1059 (57)	1095 (68)	1104 (70)	B-O symm. stretch	1161
	1235 (164)	1253 (170)	1255 (172)	B-B stretch	
	1330 (32)	1335 (40)	1340 (38)	N-H wag	
	2700 (127)	2712 (131)	2706 (125)	B-H symm. stretch	
A''	196.1 (41.0)	201 (34.0)	205 (38)	O-N-O wag	
	1130 (33)	1145 (37)	1148 (35)	B-O symm. stretch	1183
	1310 (26)	1325 (29)	133Z (27)	N-H stretch	
	2680 (146)	2685 (157)	2681 (155)	B-H asymm. stretch	

^aTaken from Ref. 15.

The values in parentheses are the IR intensities in km mol^{-1} .

Conclusion :

In this study, we made theoretical calculations of polarizability and dipole moment of boroxopyrrole and its homologues and discussed the physical mechanism contributing to these values. As a result we revealed that for the polarizability, α , the energy difference between the ground and the excited state, is one of the major factor in determining these values apart from other solvation and pH effect. The equilibrium geometries of the systems, mentioned, have different spatial arrangement with respect to pyrrole. Further, the effect of the heavy atom on the polarizability in a series of homologues is also discussed.

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