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DFT study of NLO properties of boroxine based octupolar molecules

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Abstract

First-order nonlinear optical properties of a series of octupolar boroxine derivatives are investigated using Density Functional Theory (DFT) calculations. Boroxine acting as an electron attracting core, we studied the influence, on the computed static β hyperpolarizability and on the transparency in the visible region, of the nature of donor substituting groups linked to this core and the effect of the conjugated bridge's length. The variation of this property has also been correlated to HOMO-LUMO gap and to the nature of HOMO and LUMO. The study suggests that some of the boroxine derivatives under consideration may have potential applications in the development of nonlinear optical materials.

Key words: DFT; Boroxine; Octupole; NLO; transparency.

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1- Introduction

Nonlinear optical (NLO) phenomena have been extensively studied over the last decades; molecules exhibiting large hyperpolarizabilities have a strong NLO potential and could be used, under conditions, for optoelectronics and a variety of optical devices¹⁻⁵.

Two kinds of systems bearing a significant NLO activity have been considered up to now: traditional charge transfer dipolar molecules⁶⁻⁹ or octupolar^{7, 10-13} ones. At the molecular level, the first order NLO properties (frequency doubling, Kerr effect, Electro Optical Pockels effect ...) are driven by β the first hyperpolarizability. Unfortunately most of molecules of the first kind, i.e. dipolar species, crystallize in centrosymmetric space groups, where the $\chi^{(2)}$ macroscopic susceptibility vanishes⁹⁻¹¹. In early 1990s, Zyss introduced the concept of octupolar molecule, with 1,3,5-triamino-2,4,6-trinitrobenzene (TATB)^{8,12,14} as typical example, which is characterized by a non dipolar and non-centrosymmetric planar C_{3h} or D_{3h} molecular symmetry. Since then, increasing research attention has been focused on NLO active octupolar molecules, including the extension from planar two dimensional systems, like trisubstituted benzenes (triphenylbenzenes)¹⁵, hexasubstituted benzenes (tricyanobenzenes, trinitrobenzenes, trimethoxybenzenes and phenylacetylene mesitylenes)¹⁶⁻¹⁷, 1,3,5-triazines¹⁸⁻²², to D_2 , D_3 , or T_d characterized three-dimensional ones²³⁻²⁴. An advantage of octupolar molecules is that they seem likely to crystallize in non-centrosymmetric space groups due to the lack of ground state dipole moment.

The octupolar framework provides an interesting route towards enhanced NLO responses and improved transparency. The first hyperpolarizability is a strong function of the absorption maximum especially in dipolar systems, as it can be seen from the two-level model²⁵, so that high β s are generally accompanied by absorption at large wavelengths.

Because even a small absorption at the operating wavelengths of electro-optic devices (typically 1.3 or 1.5 μm) can be detrimental, it is important to make NLO chromophores as transparent as possible. Furthermore, for frequency doubling applications one would require materials that are simultaneously transparent at the fundamental and second harmonic wavelength.

We report in this paper, a DFT computational study of series of octupolar compounds based on the boroxine ring. Indeed, despite boron inorganic crystals such as BBO (beta barium borate, β -BaB₂O₄), which is widely used in wavelength conversion devices, have long been known to display interesting NLO properties, the potentialities of molecular boroxine derivatives for NLO have not been overlooked until recently²⁶ in the context of a nonlinearity-transparency trade-off.

In this work, three octupolar series of compounds are investigated; molecules are built from the boroxine ring symmetrically grafted with three electron-releasing groups linked to the boron atoms. By increasing the electron-donating strength of substituting groups, we are aiming to increase their NLO responses. Phenyl units were selected as rigid linkers between donating substituting groups and the boroxine core so as to allow periphery-to-core intramolecular charge-transfer to take place while maintaining suitable transparency. In investigating these new compounds, the challenge is to help to the design of effective materials exhibiting both improved transparency and higher nonlinearity than TATB or the widely studied octupolar triazine derivatives.

2- Computational details

DFT theory was chosen to compute the first order hyperpolarizabilities of our systems, this choice being dictated by its reliability already discussed²⁷⁻³¹ as well as the big size of the molecules under consideration which makes impracticable sophisticated post-Hartree-Fock calculations.

For our part we made use of the Gaussian03³² package. Practically, after optimizing geometries, the β_{ijk} tensorial components are determined using Finite-Field (FF) Theory³³ implemented in the same package. So, the third rank tensor of first hyperpolarizability is described by a 3×3×3 matrix. The matrix is reduced to 10 components due to Kleinman symmetry³⁴.

Zyss et al.³⁵ have developed and discussed the tensorial nature of the first hyperpolarizability for octupolar molecules.

The relevant expression used for the calculation of the total β value is the following³⁶:

$$\beta_{\text{tot}}^2 = \beta_{\text{xxx}}^2 + \beta_{\text{yyy}}^2 + \beta_{\text{zzz}}^2 + 3\beta_{\text{xyy}}^2 + 3\beta_{\text{xzz}}^2 + \beta_{\text{yzz}}^2 + 3\beta_{\text{yxx}}^2 + 3\beta_{\text{zxx}}^2 + 3\beta_{\text{zyy}}^2 + 6\beta_{\text{xyz}}^2 \quad [1]$$

This formula is also used to compute semi-empirical AM1³⁷ β values with the MOPAC³⁸ program.

It is well documented^{14, 39-41} that considering small molecules, computed β values are very sensitive to the used basis sets, and that diffuse functions play an important role. Moreover, it is expected that the first hyperpolarizability values should also depend on the used DFT functional²⁹⁻³¹.

For our part, to assess and check our method of calculation we carried out first the computation of the NLO property under consideration at two levels of DFT, namely the two well known different hybrid functionals, B3LYP⁴² and PBE0⁴³ using different standard basis sets, 6-31G*, 6-31+G**, 6-311G**, 6-311+G**. This has been done for several test molecules, like triphenyl boroxine (TPB) and para dimethylamino-TPB (A5).

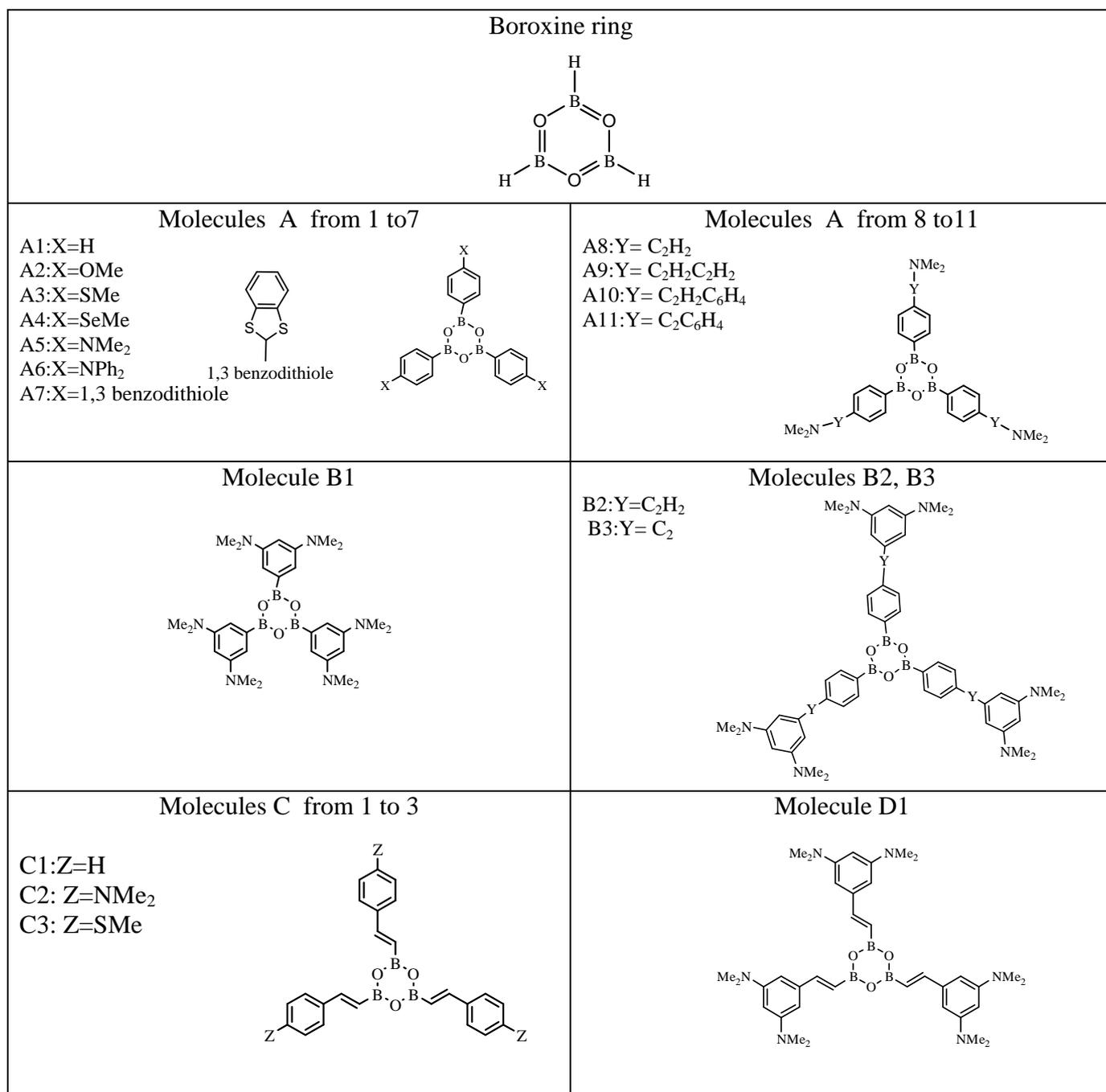
We found that the relative variation of β when changing the basis set or the functional was always less than 10%. It is worth noting that for the rather big systems under consideration the influence of the basis set extension seems to be less crucial than for small molecules. Thus, we retained the standard B3LYP/6-31G* for all our study.

In both Gaussian 03 and MOPAC packages, β_{ijk} are given in atomic units and defined via a Taylor expansion of the dipole moment. Experimental data being given using the β^X convention, the relation between the two β s is⁴⁴:

$$\beta^T = 4 \beta^X \quad [2]$$

β values reported in table 1 are within β^X convention, theoretical values are thus divided by 4 to compare them to experimental ones.

Systems under consideration



Scheme 1: Boroxine derivatives under study.

The boroxine core is stable, planar^{26, 45} in both DFT optimized and crystallographic structures, electron-deficient, and has a low aromaticity⁴⁶.

The molecules chosen in this study contain a central boroxine ring symmetrically substituted by donor groups bonded to the boron atoms in 1, 3 and 5 positions (Scheme 1).

Phenyl units were selected as rigid linkers (in A and B molecules) between the donor groups and the boroxine core so as to allow periphery-to-core intramolecular charge transfer to take place while maintaining suitable transparency. TPB, triphenyl boroxine is compound A1.

Our compounds are predominantly hypothetical, a planar geometry is assumed for most of them; such planarity is a favourable factor for conjugation and hence for a better NLO response. Almost all these molecules exhibit a C_{3h} , D_{3h} , C_3 or D_3 octupolar symmetry.

Three series are considered for discussion (scheme 1):

In series A, A2-A7, a standard donating group, i.e. NMe_2 , OMe , NPh_2 ... or 1-3 benzodithiole ends the TPB skeleton.

For A8-A11, a conjugated bridge Y is introduced at the phenyl para position between TPB and the donor X (NMe_2) group.

In series B, B1-B3, the effect of locating two NMe_2 donating groups at positions 3, 5 of the ending phenyl rings rather than one NMe_2 at para position, is studied.

In series C, C1-C3, the substituted phenyl groups are not attached directly to the boroxine core but to vinyl moieties themselves linked at positions 1, 3 and 5 of boroxine.

3- Results and discussion

In table 1 are reported computed and measured properties for the three series of compounds. Hyperpolarizabilities are in β^X ⁴⁴ convention.

In columns 3 and 4, are given the static β_{theo} and dynamical (SHG) β_{theo} AM1 results.

In columns 5 to 8, we show the static β_{theo} , the HOMO and HOMO-LUMO gap energies as well as λ_{gap} which is the wavelength corresponding to the HOMO-LUMO gap, computed at the B3LYP/6-31G* level.

Experimental values, i.e. λ_{exp} the maximum absorption wavelength and static β_{exp} (at $\omega=0$) and dynamical β_{exp} (at $\omega=1064\text{nm}$) hyperpolarizabilities are shown in the last three columns of the table.

Table 1: β first hyperpolarizability values (10^{-30} esu), HOMO, HOMO-LUMO gap energies (eV), λ_{gap} , λ_{exp} (nm) wavelengths

		AM1 calculations		B3LYP/6-31G* calculations				Experimental values		
Compd.	Sym.	β_{theo} ($\omega=0$)	β_{theo} ($\omega=1064\text{nm}$)	β_{theo} ($\omega=0$)	HOMO energy	HOMO- LUMO gap	λ_{gap}	λ_{exp}	β_{exp} ($\omega=0$)	β_{exp} ($\omega=1064\text{nm}$)
boroxine	D _{3h}	-	-	0.03	-9.19	8.70	143			
A1	C _{3h}	2	3	3	-6.77	5.62	221			
A2*	C _{3h}	5	8	7	-5.89	5.13	243	241	115	152
A3*	C _{3h}	9	17	12	-5.72	4.62	269	270	101	146
A4	C _{3h}	11	26	13	-5.54	4.42	281			
A5*	C _{3h}	10	18	13	-4.91	4.62	270	281	181	249
A6	D ₃	17	37	29	-4.99	4.00	311			
A7	C ₃	3	6	5	-5.61	3.99	312			
A8	C _{3h}	20	47	29	-4.57	3.85	323			
A9	C _{3h}	33	107	56	-4.40	3.37	369			
A10	C _{3h}	29	84	77	-4.68	3.34	372			
A11	D _{3h}	29	73	76	-4.84	3.48	357			
B1	D _{3h}	5	9	0.5	-4.46	4.06	307			
B2	C _{3h}	1	8	31	-4.68	3.27	380			
B3	D _{3h}	1	-	31	-4.76	3.33	373			
C1	C _{3h}	4	6	8	-6.07	4.49	277			
C2	C _{3h}	18	41	30	-4.77	3.87	322			
C3	C _{3h}	-	-	25	-5.49	3.98	313			
D1	C ₃	-	-	7	-4.79	3.69	338			
TATB*	D _{3h}	-	-	4						
TIATB*		-	-	6						
TPT**		-	-	4						

*From ref 26

**From ref 18 (triphenyl triazine :CPHF/6-31G)

We discuss first the B3LYP results.

As it can be seen, the boroxine ring and TPB (compound A1) display a rather low β value equal to $0.03 \cdot 10^{-30}$ and $3 \cdot 10^{-30}$ esu respectively.

Compared to widely studied triazines, TPB show comparable β value as TPT (Tri Phenyl Triazine) i.e. $4 \cdot 10^{-30}$ esu, noting however that the method of calculation is not the same⁴⁶. As it can be observed, experimental or computed β values of a boroxine derivative like A5 (X=NMe₂) is higher than TIATB ones (a soluble analogue of TATB).

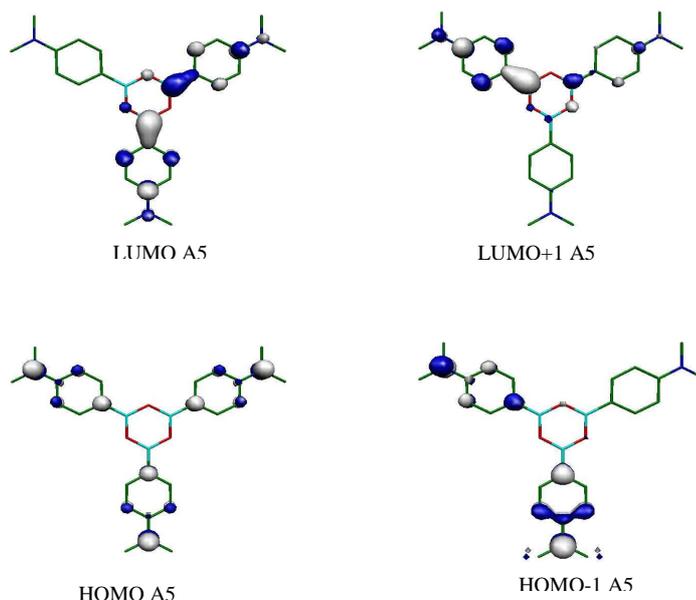
Substituting a donating group X = OMe, SMe, NMe₂, NPh₂, at the phenyl para position of TPB (scheme 1) leading respectively to compounds A2-A3, A5-A6 enhances greatly β ; for instance for A6 (X = NPh₂) β is multiplied by nine ($29 \cdot 10^{-30}$ esu) relatively to TPB. Note also that a SMe group leads to the same activity as NMe₂; indeed, A4 and A5 exhibit the same β value equal to $13 \cdot 10^{-30}$ esu. It is worth noting that for the latter molecules, the obtained β are greater than TATB and TIATB's, the latter molecules being standard 2D octupolar species.

More importantly, the magnitude of β is dependent on the bridge's length; a comparison of A5 and A8, shows that including a double C-C bond between TPB and NMe₂ increases β by a factor 2; for instance β equals 12 and $29 \cdot 10^{-30}$ esu for A5 and A8 respectively.

The replacement of a vinyl bridge by a phenyl one enhances β ; for instance β equals 56 and $77 \cdot 10^{-30}$ esu for A9 and A10 respectively. On the contrary, no difference is noticed when a C-C double bond is replaced by a triple one, as it can be seen comparing A10 and A11 which bear both a β value equal to $76-77 \cdot 10^{-30}$ esu.

It is interesting to note that a correlation exists between HOMO-LUMO gaps and β values; lower is the gap, higher is β . A7 (X = 1-3 benzodithiole) is an exception with a gap close to that of A6 (X = NPh₂) but with a β value completely different.

For A1-A6, we note also that the increase of β is related to HOMO's energy; generally, higher is the HOMO, larger is β . This HOMO (and HOMO-1) is mainly localized on the substituting X group so that its energy is indicative of the donating character of X (Scheme 2) and as expected the LUMO (LUMO+1) bears a predominating boroxine character. Strong donating groups lead to high β values.



Scheme 2: Frontier orbitals of A5

In series B, when we graft the NMe₂ donor group at meta positions 3 and 5 of TPB, like in B1, rather than at para position, β drops from $13 \cdot 10^{-30}$ esu (A5) to $0.5 \cdot 10^{-30}$ esu (B1), and when including a bridge between TPB and the substituting NMe₂ donor group, as in B2- B3, one can see that the β values are half of their A10-A11 counterparts. It is thus seen that locating a single NMe₂ donating group at the para phenyl position insures the highest β values. This result is not surprising the para position of the donating group insuring a better conjugation with the rest of the molecule.

In series C, a vinyl group is directly linked to boroxine. No remarkable enhancement of β is noticed with such a skeleton. Comparing C2 and its A8 congener, shows that their β s are equal as well as their HOMO-LUMO gaps.

For compound D1, where bridge's and position's effects are combined, it can be seen that the 3 and 5 meta positions on the phenyl ring remains a negative factor for the quadratic hyperpolarizability. Indeed, despite the presence of two donating groups such as NMe₂, and the extension of conjugation, D1 has a β of the same order of magnitude as A2 (X = OMe) , or C1, which bears no X donating group.

As in series A, we note that B and C series display the same correlation between β and HOMO-LUMO gap, but the correlation with HOMO's energies is fulfilled by C series, not by the B one, although the number of compounds is small in those series.

Finally, one can see that experimental β_{SHG} and $\beta(0)$ values are only available for A2, A3 and A5²⁶. Also, quantitative agreement between computed and experimental values is poor.

We remark also an inversion between experimental and computed values concerning A2 (X=OMe) and A3 (X=SMe). Taking into account Hammett constants, the ranking of the donating strengths is: SMe (A3) < OMe (A2) < NMe₂ (A5) which corresponds to the same ranking as $\beta_{\text{exp}}(0)$. On another hand the theoretical ranking is consistent with the donating strength of the groups as measured by the HOMO energy (table 1) showing that SMe is slightly more donating than OMe. These results agree with early investigation on these compounds²⁶. Nevertheless there is not a great difference between the experimental values of A2 and A3. Calculated values reproduce global trends; however quantitative agreement with experimental values is poor²⁶. This gives us confidence that our theoretical results are, at least qualitatively, reliable.

We investigate now the transparency of the species under consideration.

A crude estimate of the maximum absorption wavelength can be deduced from the HOMO-LUMO energy gap and is reported in table 1 (λ_{gap} values) although accurate values need the use of Time Dependent DFT (TDDFT). A very good agreement is found between experimental λ_{exp} and λ_{gap} for A2, A3 and A5²⁶. Maximum absorption wavelengths experimentally determined equal 241, 270, 281 nm, whereas computed values equal 243, 269, 270 nm respectively.

First, it is worth noting that all λ_{gap} values are in the UV region.

However, as expected, λ_{gap} values are red shifted with bridge's length, as it can be observed in A series.

In series B, no improvement in transparency is observed; on the contrary, red shift is more pronounced than in A series.

In series C, C1 compound displays a bathochromic shift about 56 nm, comparing to A1 one, so that one can expect higher values for λ_{gap} if the conjugated bridge is extended.

Finally, the compounds of series A lead to the best nonlinearity-transparency trade-off.

As it has been said before, semi-empirical calculations at the AM1 level³⁷ using the MOPAC package³⁸ have also been performed for comparison. Results (table 1) show that AM1 β_{theo} values are lower but display the same trend as B3LYP/6-31G* ones. MOPAC permits also the

computation of dynamical SHG β s. As expected, the computed $\beta(0)$ and $\beta(\omega)$ exhibit the same trend, the latter values at $\omega=1064\text{nm}$ being higher by a factor 1.5 to 2.5 than the static ones. We notice also, the same inversion of the β values between A2 and A3 when comparing to the experimental ones as observed at the DFT level of computation.

4- Conclusions

DFT calculations at the B3LYP/6-31G* were carried out on three series of octupolar boroxine based compounds. β static first-order hyperpolarizabilities have been computed and have been shown to depend on the length of the conjugated bridge linking the boroxine core to the peripheral donating groups, and the nature and the location of the latter group. Most of the studied boroxine based molecules display markedly an improved nonlinearity-transparency trade-off as compared to the prototypical organic octupolar 1, 3, 5-triamino-2, 4, 6-trinitrobenzene (TATB) or the widely studied octupolar triazine derivatives.

Considering Tri Phenyl Boroxine (TPB) as a reference skeleton, it is found that a donating group like NMe_2 must be placed at the para position of the phenyl ring in order to induce the highest β value.

Among all the studied compounds, A10 and A11, the largest molecules, characterized by an extended conjugated bridge, a NMe_2 donating group placed at a para position of the phenyl ring linked to the boroxine core, exhibit very large NLO responses, i.e. a β value equal to $77 \cdot 10^{-30}$ esu. Moreover it appears from the λ_{gap} computed values, that among the most interesting compounds several of them should be transparent in the visible region. Such compounds should be good candidates to experiment.

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