Some boric acid esters of glycerol—An *ab initio* treatment

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Some neutral acyclic and cyclic boric acid-glycerol esters and the corresponding alkoxide complexes of these cyclic esters have been treated quantum chemically at the level of 6-311G* (RHF, with and without MP2 correlation). Possible routes for the acyclic monoesters to the cyclic diesters are discussed. The terminal acyclic monoester is found to be more stable than the isomer with the internal ester group. Among the cyclic diesters, it is found that a six-membered ring is favoured energetically over the ester possessing a five-membered ring.

In aqueous solution various diols and polyols can react with boric acid to give ionic esters which have been profitably utilized in carbohydrate chemistry. In boric esters, boron is attached to three oxygen atoms, each of which has supplied one more electron for bond formation. Thus, boron has a sextet of electrons and it now lacks a pair of electrons to acquire a stable group with an alkoxide ion resulting in a salt-like compound.

\[
\begin{align*}
\text{(RO)}_3\text{B} + \text{RO} & \rightarrow \text{(RO)}_2\text{B}^-
\end{align*}
\]

As an element of Group III of the periodic table, boron has three valency electrons. In the present study, some mono and cyclic diesters of boric acid with glycerol as well as some anions (alkoxide complex) of these diesters have been studied quantum chemically at *ab initio* level.

**Methodology**

The initial geometric 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 at the restricted Hartree-Fock (RHF) level and then by *ab initio* treatment at the level of STO 3-21G* and then 6-311G* (a polarized triple zeta basis set). The geometry optimized structures were subjected to vibrational analysis (RHF, 6-311G*) for the judgment of their stabilities (no imaginary frequencies). Furthermore, all the bond lengths were thoroughly investigated. All these computations have been performed by using the Gauss-98 package program.

![Diagram](image)
Results and Discussion

The geometry optimized structures of the presently considered glycerol esters of boric acid are shown in Fig. 1. 1 and 2 are the monooesters whereas 3-5 are the cyclic diesters. Note that in 3 a five-membered, and in 4 and 5 a six-membered ring system exists.

As seen in Fig. 1, the ring in 3 is planar but the rings of 4 and 5 (six-membered ring) are not. Although, the B-O bonds are in the same plane, the six-membered ring exhibits a puckered conformation. Hence, the –OH group on the middle carbon can have axial (ax) or equatorial (eq) conformations. Also, it is to be noted that pairwise 1 and 2 or 3-5 are isomeric structures. Of all these structures, only 3 possesses a stereo center. All these structures belong to the C₃₅ molecular point group.

Stabilities of the esters

Table 1 shows the calculated total energies of the esters, complex anions and precomplexes of esters studied in the present investigation. The total energy, with or without MP2 correlation, indicates that of the isomeric structures 1 and 2, the more stable structure is 1. The formation of 1 is also obviously favoured by statistical factors because glycerol has two identical terminal –OH groups, each of which may undergo esterification yielding 1.

As for the isomeric cyclic esters, 3-5, the total energy value (with or without MP2 correlation energy) indicates that 4 is the most favourable isomer. The ester designated as 3 has planar five-membered ring and thus the ax- and eq-positions for the substituent, CH₂OH are equivalent. However, 4 and 5

![Fig. 1 — Geometry optimized structures of the studied neutral esters.](image-url)
have a puckered six-membered ring and $\alpha$- and $\epsilon$-positions for the -OH substituent on the middle carbon atom are not equivalent. Table 1 includes the total energies (with and without MP2 correlation) for the structures. As seen in Table 1, these conformers 4 and 5 are not very much energetically different but with MP2 correlation energy 4 is found to be more stable. The stability of 4, which has an axial OH group, may be attributed to capability of better hydrogen bonding in this form.

In the case of complex ester, 7, (terminal oxygens of glycerol are involved in ester linkage which prefers the chair form; the complex is designated as $E_1$(OH)), the axial and equatorial positions for the -OH group on the carbon are different. Thus, 7 ($E_1$(OH) ($\alpha\gamma$)) and 8 ($E_1$OH($\epsilon\gamma$)) conformers differ in energy, the axial one being more stable (see Table 1). This could be due to the hydrogen bonding between the axial OH group and the ring oxygens. For 6 ($E_1$(OH) the twisted form is energetically favoured (in the tables and figures this form is considered). The stability order with or without MP2 correlation is $7 > 8 > 6$.

The possible routes to the cyclic esters

If one considers the formation of cyclic ester 3, it may possibly occur via mono esters (either 1 or 2). Through complexation, various isomeric structures can be envisaged. Note that 9-11 ($HE_{12}$, $HE_2$, and $HE_{13}$ types, respectively) differ only at the protonation site, so they are all isomeric structures as well as isomeric with 1 and 2. Also, it is to be noted that the first number (i) in $HE_i$ type structures stands for the respective oxygen atom of glycerol moiety bearing the hydrogen atom, and the second number, $j$, indicates the other oxygen in the cyclic structure.

![Fig. 2 — $HE_i$ type structures.](image)

![Fig. 3 — Geometry optimized $HE_i$ type structures.](image)
On the other hand, as seen in Fig. 3, the boron-oxygen distances in 9-11 at the complexation site are longer (2.5143×10^{-10} m, 2.4959×10^{-10} m, and 2.3613×10^{-10} m, respectively) than a normal bonding distance (1.37×10^{-10} m in boric acid\(^{15}\)). So, these structures do not stand for not a real complex (although vibrational analyses, yield all positive frequencies), but represent some initial interaction (precomplexation). However, as this interaction grows, hydrogen of the alcoholic OH group may acquire protonic character. Meanwhile, the oxygen-hydrogen bond distance may elongate, and eventually the alkoxide complex of the five-membered cyclic ester 6 may be formed. Note that the formation of 7 and 8 inevitably involves the initial formation of 1 if no internal transfer of the boron moiety from 2 to 1 is assumed.

As shown by the energy data in Table 1, 10 (HE\(_{21}\)) seems to be more stable than 2 and 1. On the other hand, 11 (HE\(_{13}\)) should be more stable as compared to 1 and 2. As for the HE\(_{12} \rightleftharpoons HE\(_{21}\) equilibrium, the total energy values (with or without MP2 correlation energy) are biased towards 10 (HE\(_{21}\)). Among the group of structures whose members are represented generally by HE\(_{ij}\), the stability order is 11(HE\(_{13}\)) > 10 (HE\(_{21}\)) > 9 (HE\(_{12}\)).

Since B-O distances in 9 and 10 (2.5143×10^{-10} m and 2.4959×10^{-10} m, respectively) are elongated more as compared to that in 11 (2.3613×10^{-10} m), probably as the B-O bond is being formed, the proton is liberated (from the -OH group) to the medium forming the respective complex anions or by the removal of a water molecule the corresponding neutral esters emerge. On the other hand, both 9 and 10 turn into a common complex anion 6, whereas 11 via deprotonation generates the complex anions 7 or 8. All these anions are closed shell systems and isomeric. The calculations at the level of 6-311G* (RHF) indicate that of these three isomeric anions E\(_{13}\)(OH) is more stable. The total energy order with or without MP2 correlation is 7 > 8 > 6 (E\(_{12}\)OH(ax) > E\(_{12}\)OH(eq) > E\(_{21}\)OH, respectively. See Table 1). Figure 4 shows the geometry optimized structures for these isomeric anions.

The total energy (with MP2 correlation energy) differences between the cyclic ester 9 and its probable precursor monoesters, 1 and 2 (that is the energy difference between 9 and 1 or 2) are 199957.7 kJ/mol and 199920.2 kJ/mol, respectively. The energy difference (the total energy with MP2 correlation energy) between 6 and 1 on the one hand, and 6 and 2 on the other is 3940 kJ/mol and 3902.9 kJ/mol, respectively. Since the stability order (in terms of the total energy) for the monoesters is 1>2, the formation of 9 from 2 is less energy demanding than from 1. Mechanistically, these routes require an interaction between a free -OH group of glycerol and the boron nucleus which are represented as structures 9 and 10 (HE\(_{12}\) and HE\(_{21}\), respectively). As mentioned above 10 is more stable than 9 and the energy differences between 9 and 2 (cyclization of 2) and between 10 and 1 (cyclization of 1) are +9 and -18.3 kJ/mol (with MP2 correlation), respectively. Note that HE\(_{ij}\) type structures (9 and 10) are more stable than that of either 1 or 2, that is, the mono esters have some tendency to cyclize and cyclization of 2 is more favoured energetically. Also, the statistical factors...
Fig. 5 — Possible routes to the cyclic esters and complex ions.
favour the cyclization of 2 because in 2 the boron center is susceptible to the attack of both the terminal -OH groups of the glycerol part. Figure 3 shows the possible routes to the cyclic ester and complex anions.

The frontier molecular orbital energies

Table 2 shows the frontier molecular orbital (FMO) energies of the glycerol-boric acid esters and complex anions studied herein. The data reveal that when the -OH group on the second carbon of glycerol undergoes esterification with boric acid to form 2, the HOMO and LUMO energies are lowered as compared to the case where the terminal -OH group is involved in the esterification to form 1. The energy lowering effect is more pronounced on the HOMO than on the LUMO. In general, in the presence of electron withdrawing groups such kind of lowering of molecular orbital energy levels occurs. Since in 1 and 2 the moiety originating from boric acid is common, this effect can be attributed to a different skeletal arrangement of substituents originating from the glycerol part.

As for the cyclic esters 3-5, the data show that the LUMO energies follow the order: 3 > 2 > 4 > 1 > 5, whereas for the HOMO energies, the order is: 3 > 4 > 1 > 5 > 2. Then, the FMO energy order becomes 3 > 2 > 5 > 1 > 4. In the case of these cyclic esters, the origin of the energy lowering effect mentioned above can be attributed to both the substituent effects originating from the glycerol part, as well as the electronic effect exerted by the boron moiety. That is, the lone-pairs on oxygens involved in the ester bonding shift towards the boron atom to fill its octet hole. This effect is a kind of orbital interaction between the oxygen atoms and boron, the extent of which is subject to orientation of the orbitals in space. Thus, the ring size and conformation in the cyclic esters 3-5 (also true for 6-8) affect the molecular orbital energies.

In the case of the studied complex anions, 7 (EJ,OH(ax)) possesses comparatively lower LUMO and HOMO energy levels than 6, which has a five-membered ring. The FMO energies for these complex anions follow the order of 6 > 8 > 7.

Conclusions

Molecular orbital calculations indicate that esterification of the terminal -OH group of glycerol with boric acid leads to more stable acyclic ester (1) as compared to the one involving the internal -OH group (2). Of the cyclic diesters considered the structure possessing a six-membered ring (4 and 5) is more favourable than the ester having a five-membered ring (3) within the limitations of 6-311G* type calculations. The alkoxide complex of the cyclic esters is possible. The present study may shed some light on the formation mechanism of these type of esters as well as on some of their physicochemical properties arising from structural variations.

References