

ANTIOXIDANT POTENTIAL OF BUTYLATED HYDROXYTOLUENE (BHT) – A THEORETICAL STUDY

DALAL K. THBAYH – ANITA RÁGYANSZKI – BÉLA FISER

Abstract: Antioxidants are compounds used to prevent the thermal and photo-oxidative effects of the environment. These molecules are highly important to preserve and prolong various products. A wide variety of synthetic and natural antioxidants applied in the food and polymer industry. A good number of such molecules have phenolic character, such as in the case of butylated hydroxytoluene (BHT) which has various applications. The anti-oxidant potential of BHT has been studied by using the B3LYP density functional theory (DFT) method in combination with the 6-31G(d) basis set in gas phase. Bond dissociation enthalpies (BDEs) have been calculated for each potential hydrogen donor sites (X-H, where X = C or O) of the molecule. The antioxidant potential of the different sites has been compared by using the corresponding BDE values. The calculations indicate that the O-H group has the highest antioxidant potential (lowest BDE value, 290.3 kJ/mol) within BHT. This finding is in good agreement with previous studies. Further calculations are planned to study other antioxidant mechanisms and compounds as well. Based on the current and additional future results, new antioxidant molecules are planned to be proposed and de-signed.

Keywords: BDE, HAT, DFT, phenolic compounds, additives

INTRODUCTION

The properties of polymers depend on several factors. The resistance of a polymeric material to various conditions such as, sunlight, temperature, humidity, etc. is a fundamental issue which have to be taken into consideration during the synthesis of a product [1]. If the synthesis of the polymeric materials is not carried out carefully, the environmental factors could cause not only esthetic degradation, but potential deterioration of the mechanical properties [2]. Additives are applied to overcome these issues, which are chemicals added to the base polymer to enhance the properties (physical and chemical) of the final product [1]. These compounds are also employed to decrease cost, and maintain aesthetic qualities [3].

Several different additive types are used to enhance specific properties of the polymeric product. Polymer additives are used as plasticizers [e.g., dioctylphthalate (DOP), and tricresyl phosphate (TCP)], flame retardants [e.g., polybrominated diphenylethers (PBDES), and tris(2-chloroethyl)phosphate (TCEP)], colorants (e.g., anthraquinone, and carbon black), stabilizers (e.g., arium-zinc, and calcium-zinc), antimicrobial agents (e.g., 5-chloro-2-(2,4-dichlorophenoxy)phenol, and 4,5-dichloro-2-noctylisothiazolinone), antioxidants [e.g., butylated hydroxytoluene (BHT), and tert-butylhydroquinone (TBHQ)], and others [4].

To prevent or reduce thermal and photo-oxidative effects antioxidant (AO) additives are applied [1]. Not only polymeric materials are suffering from oxidative stress, but living organisms, and food products as well [5]. For living species, antioxidants can be either endogenous or acquired exogenously like dietary supplements (e.g., BHT) [6]. Enzymatic (e.g., superoxide dismutase) and non-enzymatic antioxidants (e.g., vitamin E, vitamin C) are the two forms of endogenous antioxidants [7].

Free radical scavenging by antioxidants could occur in three different ways, but each of these will lead to the donation of a hydrogen atom ($H\bullet$) to the free radical. The direct hydrogen atom ($H\bullet$) transfer (HAT) to the radical is a one-step mechanism. The other two includes two steps, either first a single electron transfer followed by a proton (H^+) transfer (SET-PT), or vice versa, H^+ moves first and after the electron (SPLET) from the antioxidant to the radical [8]. To study these mechanisms several physico-chemical properties can be measured or computed. Such properties are the bond dissociation enthalpy (BDE), ionization potential (IP), proton dissociation enthalpy (PDE), proton affinity (PA), and electron transfer enthalpy (ETE) [9–12].

Antioxidant molecules can be natural and synthetic compounds [6]. The widespread environmental issues forced producers to consider replacing commonly used synthetic materials with natural alternatives. However, to find environmentally friendly, and effective alternatives of the commonly used additives is difficult to implement and requires a lot of planning and research.

Environmentally friendly antioxidant polymer additives will be proposed and/or designed. Therefore, the antioxidant potential of a widely used food additive, butylated hydroxytoluene is studied. BHT is extensively used as an additive in the food industry and has been utilized in a variety of food applications [7]. It is also commonly used as a positive control in the measurement of antioxidant activity due to its AO capabilities and simple structure [13, 14]. Our aim is to carry out a theoretical study on the antioxidant activity of various antioxidants (*Figure 1*), starting with BHT and use the acquired results in AO design in the future.

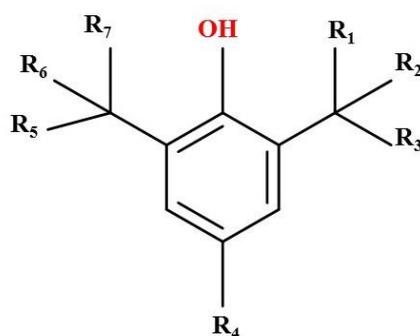


Figure 1

General chemical structure of common antioxidants.

Based on the calculations, new AOs can be designed and later tested as polymer additives to pave the way for a more environmentally friendly polymer composition.

1. MATERIALS AND METHODS

All calculations have been carried out by using the Gaussian 09 program package [15]. The B3LYP density functional theory (DFT) method [16, 17] in combination with the 6-31G(d) basis set has been used to optimize the studied molecule and the corresponding radical species in gas phase. The bond dissociation enthalpies (BDE) of each potential hydrogen donor sites of the molecule have been computed by considering the following hypothetical reaction:



where 'A' is the antioxidant molecule, while $A\cdot$ and $H\cdot$ are the corresponding radical and hydrogen atom which will form after the dissociation of an X-H ($X = C, \text{ or } O$) bond.

2. RESULTS AND DISCUSSION

Direct hydrogen atom ($H\cdot$) transfer (HAT) mechanism is considered. In this case, the molecule donates a hydrogen atom to the free radical and thus, the reactive compound is neutralized. To compare the antioxidant activity of the different groups, bond dissociation enthalpies (BDEs) have been calculated for each potential hydrogen donor sites (X-H, where $X = C, \text{ or } O$) of the molecule. The different sites have been compared by using the corresponding BDE values. The bond lengths vary between 0.964 Å and 1.097 Å within the optimized structure of the molecule (*Figure 2*).

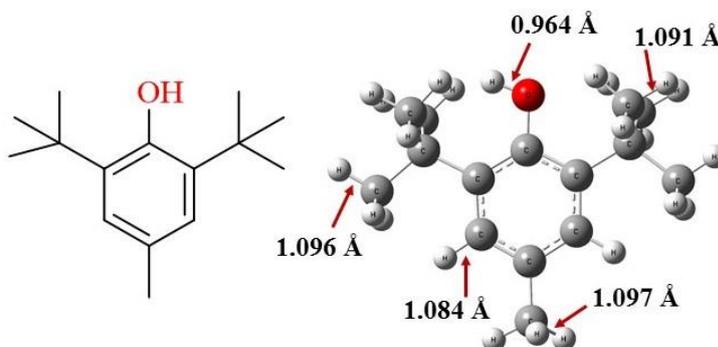


Figure 2

2D and 3D structure of butylated hydroxytoluene (BHT). The 3D structure has been optimized at the B3LYP/6-31G(d) level of theory in gas phase. The corresponding bond lengths are also depicted.

The radicals were prepared from the optimized BHT molecule by removing one hydrogen atom from each potential sites (*Figure 3*). All in all, six radicals have been created and the structures have been optimized (*Figure 3*).

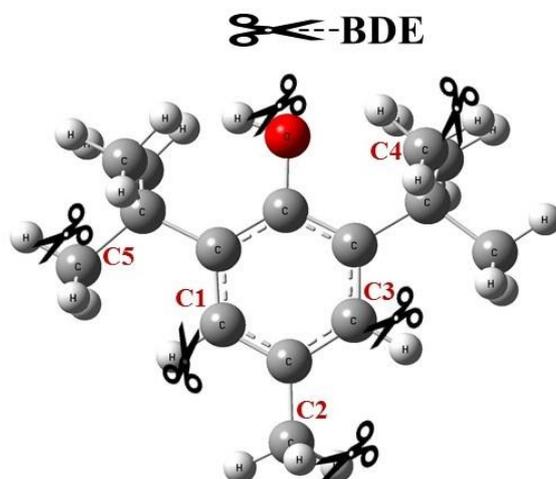


Figure 3
Hydrogen atom donor sites of butylated hydroxytoluene (BHT)

By using the computed thermodynamic properties of BHT and the corresponding radicals, BDE values of the functional groups have been computed along with zero-point corrected relative energies (ΔE_0) and relative Gibbs free energies (ΔG) according to the above-mentioned hypothetical reaction (see Materials and Methods and Table 1).

Table 1
Bond Dissociation enthalpies (BDEs) of butylated hydroxytoluene (BHT), zero-point corrected relative energies (ΔE_0), and relative Gibbs free energies (ΔG). All structures have been computed at the B3LYP/6-31G(d) level of theory in gas phase

X-H position	ΔE_0	ΔG	BDE	Bond length
				Å
O-H	285.1	254.7	290.3	0.964
C1-H	443.0	412.3	449.6	1.084
C2-H	358.4	332.3	363.2	1.097
C3-H	443.0	412.3	449.6	1.084
C4-H	390.4	361.7	395.8	1.091
C5-H	411.9	380.4	419.5	1.096

The BDEs of the C-H bonds within BHT cover a wide range starting from 363.2 and reaching to 449.6 kJ/mol (Table 1, Figure 4). The weakest within the C-H bonds is C2-H (1.097 Å) and it is located on the methyl group which is in the para position and has a BDE of 363.2 kJ/mol (Figure 4). The removal of a hydrogen atom from the aromatic ring of BHT is unfavourable as the strongest bonds are C1-H and C3-H (1.084 Å), which have identical BDE values (449.6 kJ/mol). The results indicate that

shorter bond length can be associated with larger bond dissociation enthalpy and thus, stronger bond. All in all, the BDE values indicate that the O-H is the weakest (290.3 kJ/mol) within the studied set of bonds (*Table 1, Figure 4*). This finding is in good agreement with previous studies [7].

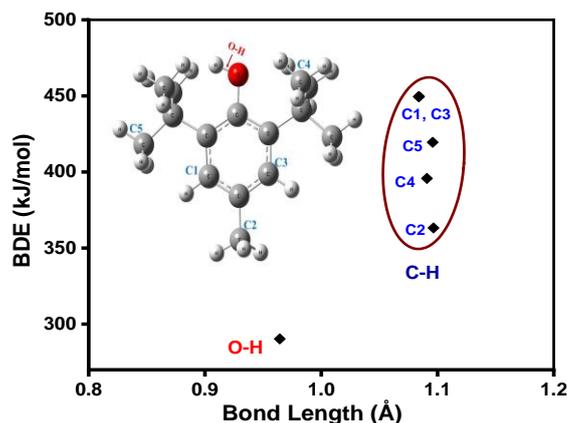


Figure 4

Bond dissociation enthalpy (BDE) vs. bond length diagram of butylated hydroxytoluene (BHT). All structures have been computed at the B3LYP/6-31G(d) level of theory in gas phase.

The lower the BDE value, higher the ability of the antioxidant to donate its hydrogen atom to free radicals. Thus, based on these results, it is obvious that the hydroxyl group contributes mostly to the antioxidant activity of BHT compared to C-H bonds when the HAT mechanism is considered. However, C-H bonds (e.g., C2-H) can also play a role in the antioxidant process and thus, the antioxidant potential of BHT is significant.

CONCLUSION

The antioxidant potential of butylated hydroxytoluene (BHT) have been studied by using computational chemical tools and considering the direct hydrogen atom (H•) transfer (HAT) mechanism. To reveal the antioxidant activity of the different groups, bond dissociation enthalpies (BDEs) have been calculated for each potential hydrogen donor sites of the molecule. All in all, seven potential hydrogen donor sites were considered, and their BDE values were compared.

The weakest within the C-H bonds is located on the methyl group which is in the para position and has a BDE of 363.2 kJ/mol. The removal of a hydrogen atom from the aromatic ring of BHT is unfavourable as the strongest C-H bonds indicates (449.6 kJ/mol). All in all, the O-H is the weakest (290.3 kJ/mol) within the studied set of bonds and thus, the hydroxyl group contributes mostly to the antioxidant activity of BHT when the HAT mechanism is considered. However, C-H bonds can also play a role in the antioxidant process and thus, the antioxidant potential of BHT is signifi-

cant. Additional calculations are planned to study the performance of BHT in other antioxidant mechanisms (SET-PT and SPLET). Furthermore, additional molecules will also be studied to explore their potential application as antioxidant additives in polymer synthesis. Based on the current and future results, new AO additives are planned to be proposed and designed.

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