



King Saud University
Arabian Journal of Chemistry

www.ksu.edu.sa
www.sciencedirect.com



ORIGINAL ARTICLE

Effect of donor and acceptor groups on radical scavenging activity of phenol by density functional theory

Abdullah G. Al-Sehemi ^{a,b,*}, Ahmad Irfan ^{a,*}

^a Department of Chemistry, Faculty of Science, King Khalid University, P.O. Box 9004, Abha 61413, Saudi Arabia

^b Unit of Science and Technology, Faculty of Science, King Khalid University, P.O. Box 9004, Abha 61413, Saudi Arabia

Received 7 July 2012; accepted 15 June 2013

KEYWORDS

Density functional theory;
Molecular properties;
Bond dissociation enthalpy;
Adiabatic ionization
potential

Abstract Ground state geometries of Phenol, p-nitrophenol, p-fluorophenol, p-methylphenol, p-methoxyphenol, p-aminophenol, p-hydroxybenzotrile, 1-(4-hydroxy-phenyl)-ethanone, p-hydroxybenzoic acid and p-dimethylaminophenol have been optimized by using the density functional theory (DFT) at four different levels of theories; B3LYP/6-31G*, B3LYP/6-31+G*, B3LYP/6-311G* and B3LYP/6-311++G**. The frequencies and charged species of all the investigated compounds have been calculated at the same level of theories. To explain the molecular properties energy gap, electronegativity (χ), hardness (η), electrophilicity (ω), softness (S) and electrophilicity index (ω_i) have been computed. Hydrogen atom transfer and one-electron transfer mechanisms have been discussed to shed light on the radical scavenging activity.

© 2013 Production and hosting by Elsevier B.V. on behalf of King Saud University.

1. Introduction

Oxidative stress induced by reactive oxygen species and reactive nitrogen species such as the superoxide anion radical, hydroxyl radical, lipid peroxyl radical, or peroxyxynitrite, can cause damage to cellular proteins, membrane lipids and nucleic acids, where this process has been implicated in the pathogenesis of various diseases, including coronary heart disease and

some forms of cancer (Pietta, 2000). Flavonoids are the most important class of polyphenolic compounds, which in addition to their important biological roles in plant pigmentation, nitrogen fixation, and chemical defense possess anti-cancer, anti-inflammatory, antibacterial, antiviral, and antiallergic properties that are a consequence of their antioxidant properties (Aron and Kennedy, 2008; Halliwell, 2007; Manach et al., 2005; Rosane et al., 2006). Radical scavenging activity of different compounds has been studied intensively in recent years (Mandade et al., 2011; Liu et al., 2011; Xue et al., 2012; Aksoy et al., 2013; Stepanic et al., 2013; Yu et al., 2013).

Polyphenol compounds such as protocatechuic acid, caffeic acid and a variety of flavonoids are present in fruits and vegetables and are an integral part of the human diet. It is already known that dietary polyphenols show potent antiradical ability. The radical scavenging abilities of these compounds depend greatly on the number and arrangement of phenolic hydroxyl groups. Recently, theoretical methods especially the

* Corresponding authors at: Department of Chemistry, Faculty of Science, King Khalid University, P.O. Box 9004, Abha 61413, Saudi Arabia. Tel.: +966 72418632; fax: +966 72418426.

E-mail addresses: agmasq@gmail.com (A.G. Al-Sehemi), irfaahmad@gmail.com (A. Irfan).

Peer review under responsibility of King Saud University.



Production and hosting by Elsevier

density functional theory (DFT) method, have been successfully used to evaluate chemical properties, such as bond dissociation enthalpy (BDE) and the adiabatic ionization potential (IP) of polyphenol compounds and to elucidate the structure–activity relationship for phenolic antioxidants (Antoncjak, 2008). Furthermore, the study of the electronic and molecular properties is of great importance that helps to understand the mechanism of the antioxidant activity of these compounds.

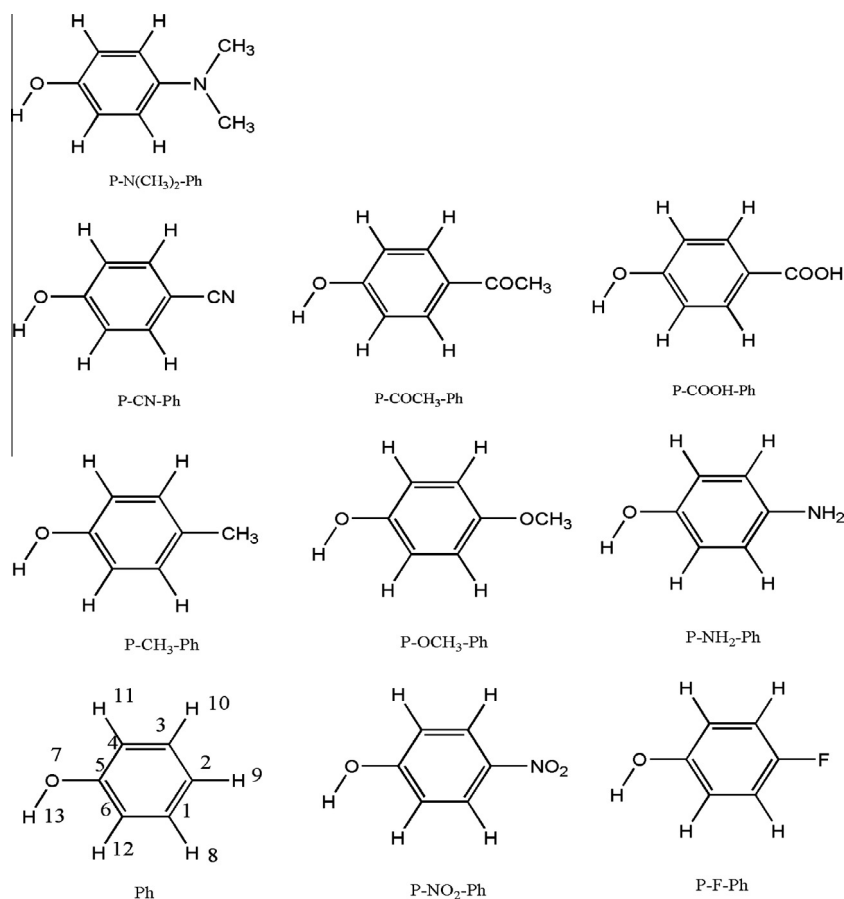
The antioxidant activity of the phenolic constituents is related to their structures. However, to the best of our knowledge, no calculation about the antioxidant activity has been reported so far for Phenol (Ph), p-nitrophenol (p-NO₂-Ph), p-fluorophenol (p-F-Ph), p-methylphenol (p-CH₃-Ph), p-methoxyphenol (p-OCH₃-Ph), p-aminophenol (p-NH₂-Ph), p-hydroxybenzotrile (p-CN-Ph), 1-(4-hydroxy-phenyl)-ethanone (p-COCH₃-Ph), p-hydroxybenzoic acid (p-COOH-Ph) and p-dimethylaminophenol (p-N(CH₃)₂-Ph), see Scheme 1. In this work, the structural, electronic and molecular properties were investigated at the density functional theory level. Our aim is to shed light on the radical scavenging activity and reveal their scavenging capacity through calculation of proper molecular descriptors. Bond dissociation enthalpy (BDE) and ionization potential (IP) values have been used as indicators of the ease by which these molecules can deactivate free radicals. The present study deals with the effect of donor and acceptor groups on the radical scavenging activity and antioxidant nature. This study would also help the experimentalists to synthesize new antioxidant polyphenol materials.

2. Computational detail

Generally two main mechanisms are reported for the radical scavenging processes of chain-breaking antioxidant (ArOH) (Wright et al., 2001; Leopoldini et al., 2004; Belcastro et al., 2006): H-atom transfer (Eq. (1)) and one-electron transfer (Eq. (2)):



Both mechanisms are important for the scavenging activity of reactive species by an ArOH in chemical or biological system and may occur in parallel. In the H-atom transfer, a free radical R removes a hydrogen atom from the antioxidant ArOH. The efficiency of the antioxidant ArOH depends on the stability of the radical ArO, which in turn is determined by the number of hydrogen bonds, conjugation, and resonance effects. The reactivity of an ArOH can be estimated by calculating the O–H bond dissociation enthalpy (BDE), where the lower the BDE value the higher is the expected activity. The antioxidants give an electron to the free radical in the one-electron transfer mechanism. Here, the radical cation arising from the electron transfer must be stable. In this case, scavenging activity can be evaluated by the adiabatic ionization potential (IP). Molecules with the low IP and BDE values are expected to have high activity. Thus, in the present study BDE and IP values were used as molecular descriptors in an effort to explain



Scheme 1 The studied systems of phenol with labeling and its derivatives.

the radical scavenging activity of compounds. All calculations were performed by Gaussian 09 code (Frisch et al., 2009). The ground state geometries have been optimized at the B3LYP/6-31G*, B3LYP/6-31+G*, B3LYP/6-311G* and B3LYP/6-311++G** levels of theories. Harmonic vibrational frequency calculations were performed at the B3LYP/6-31G*, B3LYP/6-31+G*, B3LYP/6-311G* and B3LYP/6-311++G** levels of theories for both parent (ArOH) molecules and radicals (ArO and ArOH⁺), to characterize all their conformations as minima or saddle points and to evaluate the zero-point energy (ZPE) corrections, which we have included in all the relative energies, BDE, and IP. The BDE values in the gas phase at 298 K were calculated according to the formula $BDE = H_{rad} + H_{hyd} - H_p$, where H_{rad} is the enthalpy of the radical generated by H-abstraction, H_{hyd} is the enthalpy of the H-atom, and H_p is the enthalpy of the parent molecule. The adiabatic IP values were determined according to the equation $IP = E_{cr} - E_p$, where p and cr indicate the parent molecule and the corresponding cation radical generated after electron transfer. The DFT-based reactivity descriptors were obtained from the Eqs. (3)–(7) which play an important role in many areas of research (Kohn et al., 1996; Parr and Pearson, 1983; Chattaraj et al., 1991).

Mulliken electronegativity (χ) was calculated from the following equation:

$$\chi = (E_{HOMO} + E_{LUMO})/2 \quad (3)$$

Hardness (η) was calculated from the following equation:

$$\eta = (E_{LUMO} - E_{HOMO})/2 \quad (4)$$

Electrophilicity (ω) was calculated from the following equation:

$$\omega = (E_{HOMO} + E_{LUMO}/2)^2/2\eta \quad (5)$$

Softness (S) was calculated from the following equation:

$$S = 1/2\eta \quad (6)$$

Electrophilicity index (ω_i) was calculated from the following equation:

$$\omega_i = \mu^2/2\eta \quad (7)$$

3. Results and discussions

3.1. Geometries

The geometrical parameters at B3LYP/6-31G*, B3LYP/6-31+G*, and B3LYP/6-311G* levels of theories have been tabulated in Table S1. The bond lengths at all the levels of theories are analogous which revealed that basis set has no significant effect on the bond lengths. The O7–C5 bond length is shortened in p-NO₂-Ph while is lengthened in p-OCH₃-Ph and p-NH₂-Ph. The C1–C2 and C2–C3 also lengthen in p-OCH₃-Ph and p-NH₂-Ph compared to parent molecule. But the effect toward lengthening or shortening is not so significant.

Previously, it has been shown that C–O bond has some double bond character due to which hydrogen atom lies in the plan of benzene (Pauling, 1960). We have observed in phenol and its derivatives that hydrogen atom lies in the plan of benzene revealing (a) C–O bond has double bond character, (b) the optimized geometries are reliable.

The geometrical parameters of phenol have been computed by using B3LYP/6-311++G** (Rappoport, 2003) and MP2/6-31G** (Yamashita and Ouchi, 1979) levels of theories, previously. The O7–H13, O5–C7, C1–C2 and C2–C3 have been observed to be 0.964, 1.371, 1.392 and 1.395 Å for phenol, respectively at B3LYP/6-311++G** level of theory computed in the present investigations which are in good agreement with the previous studies by Rappoport, i.e., O7–H13, O5–C7, C1–C2 and C2–C3 have been observed to be 0.963, 1.370, 1.393 and 1.396 Å. The O7–H13, O5–C7, C1–C2 and C2–C3 have been observed to be 0.973, 1.374, 1.393 and 1.396 Å, respectively at MP2/6-31G** level of theory. Moreover, experimentally C–O bond length has been observed to be 1.360 Å [ddd] which is in good agreement with our computed data at all the levels of theories. Our computed data at all the levels of theories are in good agreement with the computed data at B3LYP/6-311++G** and MP2/6-31G** levels of theories.

3.2. Natural bond analysis

The Natural bond analysis has been presented in Table S2. The numbering scheme can be found in Figure S1. The C2 is the position where different electron donor or acceptor groups have been attached. The charge is more negative for p-CH₃-Ph among other derivatives but less than the parent molecule. The C5 is more positive for p-NO₂-Ph; the trend from higher to lower charge density at C5 position has been observed as p-NO₂-Ph > Ph > p-CH₃-Ph > p-F-Ph > p-OCH₃-Ph > p-NH₂-Ph. In p-NO₂-Ph charge at O7 is the smallest while in p-NH₂-Ph highest.

3.3. Molecular properties

Fig. 1 illustrates the distribution pattern of the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO). The HOMO is delocalized on entire molecules and lone pair of electron on the oxygen atoms while the LUMO is of antibonding character with π^* distributed on core of the systems in parent molecule. In p-NO₂-Ph the HOMO is delocalized at the benzene ring, oxygen of hydroxyl and nitro group while LUMO is localized at nitro, benzene ring as well as oxygen lone pair participating in the formation of LUMO. In p-NH₂-Ph the HOMO is delocalized at the benzene ring and oxygen of the hydroxyl group while LUMO at the benzene ring. In p-CN-Ph, the HOMO and LUMO are distributed on the backbone. In p-COCH₃-Ph and p-COOH-Ph, the HOMOs are delocalized on benzene and oxygen atoms are taking part in the formation of HOMOs while LUMOs are distributed on the entire systems. In p-N(CH₃)₂-Ph, the HOMO is distributed on the entire system while LUMO is localized on ring. Other studied compounds have a similar distribution pattern of the frontier molecular orbitals (HOMOs and LUMOs) similar to phenol.

The HOMOs, LUMOs, energy gap, electronegativity (χ), hardness (η), electrophilicity (ω), softness (S) and electrophilicity index (ω_i) at the B3LYP/6-31G*, B3LYP/6-31+G*, B3LYP/6-311G* and B3LYP/6-311++G** levels of theories have been presented in Tables 1 and S3. The HOMO energy (E_{HOMO}), LUMO energy (E_{LUMO}) and HOMO–LUMO energy gap (E_{gap}) have been used as an indicator of kinetic stability of the molecule as well. It has been observed that the trend

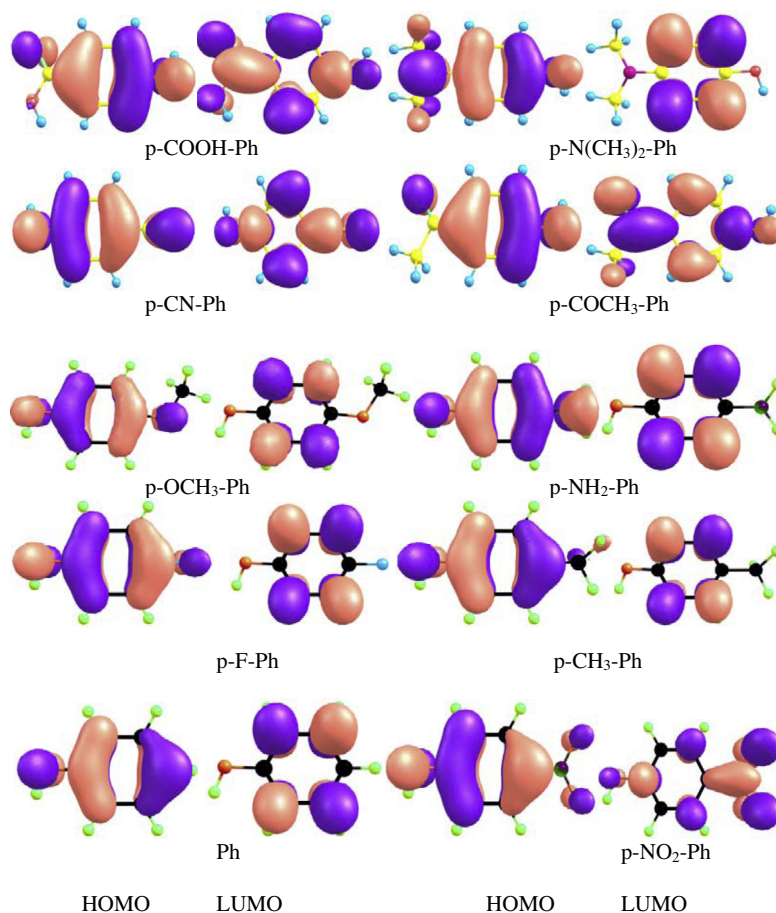


Figure 1 The distribution pattern of the HOMOs and LUMOs of the studied compounds.

Table 1 Different descriptors obtained at B3LYP/6-311 + G** level of theories.

| | Ph | p-NO ₂ -Ph | p-F-Ph | p-CH ₃ -Ph | p-OCH ₃ -Ph | p-NH ₂ -Ph |
|-------------------|---------|-------------------------|-----------|--|------------------------|-----------------------|
| E_{HOMO} | -6.39 | -7.35 | -6.45 | -6.14 | -5.76 | -5.42 |
| E_{LUMO} | -0.57 | -2.74 | -0.93 | -0.54 | -0.58 | -0.51 |
| E_{gap} | 5.82 | 4.61 | 5.52 | 5.60 | 5.18 | 4.91 |
| χ | 3.48 | 5.04 | 3.69 | 3.34 | 3.17 | 2.96 |
| η | 2.91 | 2.30 | 2.76 | 2.80 | 2.59 | 2.45 |
| ω | 1.74 | 2.52 | 1.84 | 1.67 | 1.58 | 1.48 |
| S | 0.14 | 0.10 | 0.13 | 0.15 | 0.16 | 0.17 |
| ω_i | 2.08 | 5.52 | 2.46 | 1.99 | 1.94 | 1.79 |
| | p-CN-Ph | p-COCH ₃ -Ph | p-COOH-Ph | p-N(CH ₃) ₂ -Ph | | |
| E_{HOMO} | -7.01 | -6.77 | -7.05 | -5.11 | | |
| E_{LUMO} | -1.55 | -1.71 | -1.66 | -0.38 | | |
| E_{gap} | 5.46 | 5.06 | 5.39 | 4.73 | | |
| χ | 4.28 | 4.24 | 4.35 | 2.74 | | |
| η | 2.73 | 2.53 | 2.69 | 2.36 | | |
| ω | 2.14 | 2.12 | 2.18 | 1.37 | | |
| S | 0.12 | 0.12 | 0.11 | 0.18 | | |
| ω_i | 3.35 | 3.55 | 3.51 | 1.59 | | |

of the HOMOs, LUMOs, energy gap, electronegativity (χ), hardness (η), electrophilicity (ω), softness (S) and electrophilicity index (ω_i) at all the levels of theories is similar. Generally, E_{HOMO} and E_{LUMO} of electron donor substituted derivatives

are higher while acceptor ones are smaller compared to phenol. The energy gap of p-CH₃-Ph, p-OCH₃-Ph and p-NH₂-Ph is higher while p-NO₂-Ph is smaller than the parent molecule. The χ and ω are smaller for derivatives where the donor group

is substituted while larger for those in which the acceptor group is introduced than that of the parent molecule. We have also observed that HOMO and LUMO have almost equal charge density; similarly HOMO-1 charge density is similar to HOMO. The LUMO + 1 has higher charge density than the LUMO in all the studied compounds except p-nitro phenol in which HOMO-1 has higher charge density than HOMO and LUMO, see Fig. 2 and S2. Free radical-scavenging activity of various phenolic antioxidants is also strictly related to the distribution of the HOMO orbital. The molecules with a lower energy of the HOMO orbital having weaker electron donating ability revealed that p-NO₂-Ph have lower electron donating ability compared to p-CH₃-Ph, p-OCH₃-Ph and p-NH₂-Ph. Besides, the electronic density distribution in these orbitals permits the prediction of the most probable sites in the molecules investigated which can be easily attacked by free radicals and other reactive agents.

The chemical hardness is a measure of resistance to charge transfer while the electronegativity is a measure of the tendency to attract electrons by an atom in a chemical bond which is defined as negative of the chemical potential in DFT. The electrophilicity index ω represents the stabilization energy of the system and determines the affinity for the electrons. The molecular properties that were computed for each variable are shown in Tables 1 and S3 which clearly indicate that p-NO₂-Ph is capable of attracting an electron instead of giving them while p-CH₃-Ph, p-OCH₃-Ph and p-NH₂-Ph are proficient of giving electron rather than capturing which in turn is an indication of their antioxidant ability.

We have also investigated the effect of donor and acceptor groups on the Mulliken electronegativity, Hardness, Electrophilicity, Softness, and Electrophilicity index. Generally, the electron donor group lowered while the electron withdrawing group increased the χ , and ω compared to phenol. Here we have compared the effect of donor or acceptor groups on different chemical descriptors with phenol. The η decreased by introducing the donor or acceptor group. Significant effect of decreasing the η has been observed for those derivatives in which strong deactivating (nitro) or activating (NH₂) groups have been substituted. The reverting effect has been observed on the S which increases by substituting the nitro or NH₂ groups. The significant effect of augmenting the ω has been observed for the nitro substituent derivative while it decreases for OCH₃ one.

3.4. Hydrogen atom transfer mechanism

By hydrogen abstraction, we obtained radicals in which the hydrogen atoms have been abstracted from the hydroxyl group. Single radical cation for each parent molecule was obtained, see Fig. 3. We have presented the BDE values in Table 2 that describe the hydrogen atom donating ability. The BDE values have been compared to the phenol BDE (Wright et al., 2001) as well. The imperative position for hydrogen atom transfer is hydroxyl.

It can be seen that the BDE values computed at B3LYP/6-31G*, B3LYP/6-31 + G*, B3LYP/6-311G* and B3LYP/6-311 + G** levels of theories showed a similar trend of decreasing or increasing by substituting the donor or acceptor groups. Moreover, no significant effect has been observed in BDE value by changing the basis set. Our computed

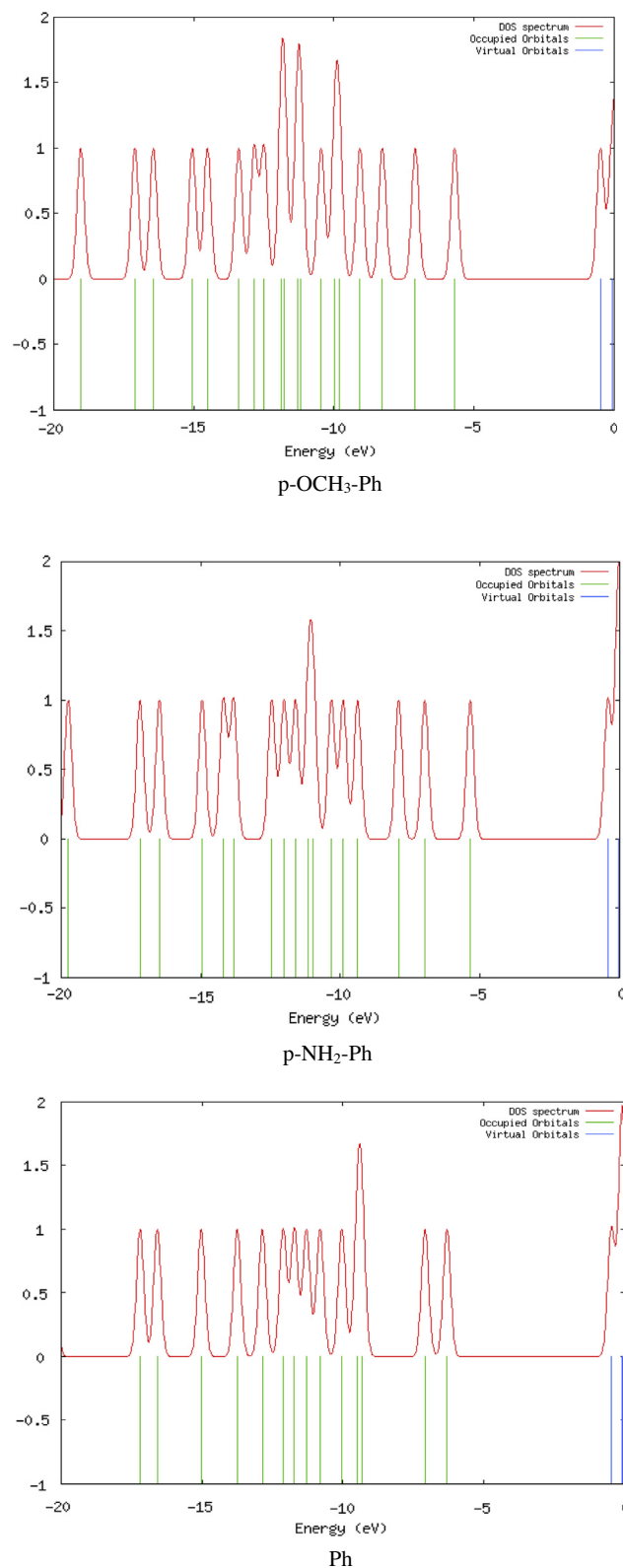


Figure 2 The density of state of the phenol and some of its derivatives.

parameters of phenol are also in good agreement with the previous study (Wright et al., 2001). Generally, BDE is enhanced by substituting the electron withdrawing group at para posi-

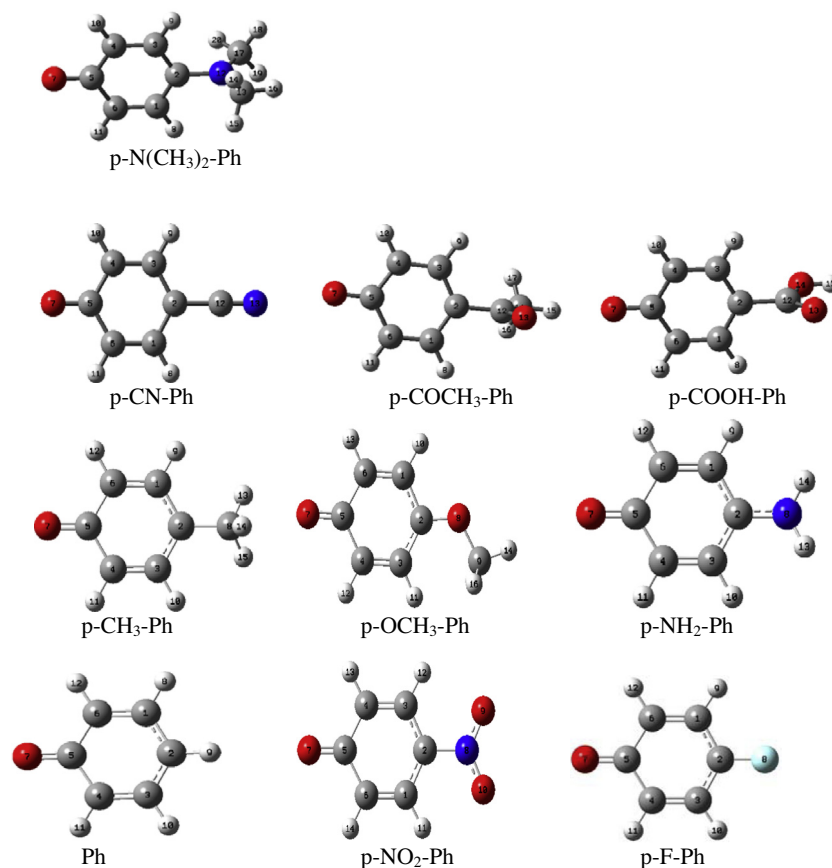


Figure 3 The optimized structures of the radical cations investigated in the present study.

tion while the electron donor group at para position lowers the BDE. The significant effect has been observed for p-amino phenol which revealed that abstraction of hydrogen would be favorable to enhance the antioxidant activity. The substitution of NH_2 , OCH_3 and $\text{N}(\text{CH}_3)_2$ are at para positions. Furthermore, the BDE of p-F-Ph and p- CH_3 -Ph is also smaller than phenol revealing better antioxidant than parent molecule. From Table 2, it can be seen that the BDE values of p- CH_3 -Ph, p- OCH_3 -Ph, p- NH_2 -Ph and p- $\text{N}(\text{CH}_3)_2$ -Ph are smaller than the phenol which revealed that aptitude toward the donating of the hydrogen atom/atoms improved in phenolic hydroxyls when the donor group is substituted. Moreover, we have observed that in nitro, cyano, and carboxylic substituted derivative, charge density in LUMO is localized on oxygen of hydroxyl due to which abstraction of hydrogen from p- NO_2 -Ph, p-CN-Ph and p-COOH-Ph would be difficult. On the other hand in p- CH_3 -Ph, p- OCH_3 -Ph, p- NH_2 -Ph and p- $\text{N}(\text{CH}_3)_2$ -Ph derivatives oxygen of hydroxyl does not participate in the formation of LUMO which would ease the abstraction of hydrogen leading to lower BDE. Finally, Hydrogen atom transfer mechanism would be favorable in the derivatives where the donor group has been substituted at para position.

3.5. Single electron transfer mechanism

The scavenging of free radicals by polyphenols may be achieved by donating a single electron. The IP is an important physical factor revealing the range of electron transfer. According to the one-electron transfer, an electron is removed from the HOMO of the parent molecules, giving rise to radical cations. The investigated compounds have planer radical cations revealing there would be entire conjugation. The hydrogen bonds similar to the parent molecule are contributing to auxiliary stabilization. The IP values for p- OCH_3 -Ph, p- NH_2 -Ph and p- $\text{N}(\text{CH}_3)_2$ -Ph are 20, 30 and 26 kcal/mol smaller than phenol illuminating electron transfer mechanism for the scavenging of free radicals. The electron transfer of p- NH_2 -Ph would be similar to that of other flavonoids which have 30–40 kcal/mol smaller IP values than phenol (Ji et al., 2005). Noteworthy effect has been observed in p- OCH_3 -Ph, p- NH_2 -Ph and p- $\text{N}(\text{CH}_3)_2$ -Ph. The low IP value compared to phenol revealed that p- CH_3 -Ph, p- OCH_3 -Ph, p- NH_2 -Ph and p- $\text{N}(\text{CH}_3)_2$ -Ph would be better antioxidant materials (see Table 2).

4. Conclusions

The HOMOs are delocalized on entire molecules and lone pair of electron on the oxygen atoms while LUMOs are of antibonding character with π^* distributed on the core. The energy

Table 2 The BDE and IP of phenol^a and its derivatives in kcal/mol.

| Comp. | Ph | p-NO ₂ -Ph | p-F-Ph | p-CH ₃ -Ph | p-OCH ₃ -Ph | p-NH ₂ -Ph |
|-------------------------|--------|-----------------------|-------------------------|-----------------------|---------------------------------------|-----------------------|
| <i>B3LYP/6-31G*</i> | | | | | | |
| BDE | 69.69 | 73.64 | 67.97 | 68.02 | 64.98 | 61.96 |
| IP | 184.74 | 202.80 | 183.38 | 176.82 | 165.10 | 154.45 |
| Comp. | | p-CN-Ph | p-COCH ₃ -Ph | p-COOH-Ph | p-(NCH ₃) ₂ Ph | |
| BDE | | 71.64 | 71.36 | 72.26 | 61.25 | |
| IP | | 195.91 | 187.97 | 193.38 | 146.50 | |
| <i>B3LYP/6-31+G*</i> | | | | | | |
| Comp. | Ph | p-NO ₂ -Ph | p-F-Ph | p-CH ₃ -Ph | p-OCH ₃ -Ph | p-NH ₂ -Ph |
| BDE | 70.27 | 74.43 | 68.84 | 78.44 | 65.37 | 62.11 |
| IP | 190.44 | 210.20 | 190.66 | 182.22 | 171.09 | 160.85 |
| Comp. | | p-CN-Ph | p-COCH ₃ -Ph | p-COOH-Ph | p-(NCH ₃) ₂ Ph | |
| BDE | | 72.23 | 72.03 | 73.07 | 61.35 | |
| IP | | 201.63 | 194.10 | 199.92 | 152.10 | |
| <i>B3LYP/6-311G*</i> | | | | | | |
| Comp. | Ph | p-NO ₂ -Ph | p-F-Ph | p-CH ₃ -Ph | p-OCH ₃ -Ph | p-NH ₂ -Ph |
| BDE | 70.16 | 73.95 | 68.52 | 67.77 | 65.21 | 61.78 |
| IP | 189.20 | 206.62 | 188.59 | 181.12 | 169.34 | 158.33 |
| Comp. | | p-CNvPh | p-COCH ₃ -Ph | p-COOH-Ph | p-(NCH ₃) ₂ Ph | |
| BDE | | 72.01 | 71.75 | 72.67 | 61.34 | |
| IP | | 200.41 | 192.48 | 197.97 | 150.70 | |
| <i>B3LYP/6-311++G**</i> | | | | | | |
| Comp. | Ph | p-NO ₂ -Ph | p-F-Ph | p-CH ₃ -Ph | p-OCH ₃ -Ph | p-NH ₂ -Ph |
| BDE | 70.16 | 73.95 | 68.52 | 67.77 | 65.21 | 61.78 |
| IP | 192.09 | 209.79 | 204.26 | 183.44 | 172.38 | 162.42 |
| Comp. | | p-CN-Ph | p-COCH ₃ -Ph | p-COOH-Ph | p-(NCH ₃) ₂ Ph | |
| BDE | | 76.51 | 76.18 | 77.31 | 63.51 | |
| IP | | 203.11 | 195.05 | 201.20 | 166.49 | |

^a The BDE and IP is 83 and 192 kcal/mol from Wright et al., 2001.

gaps of newly designed derivatives are smaller than the parent molecule at B3LYP/6-311++G** level of theory. The χ , and ω are smaller for the derivatives where the donor group is substituted while higher for derivatives in which the strong electron deactivating group is introduced as compared to the parent molecule. We have also observed that HOMO and LUMO have almost equal charge density. The p-NO₂-Ph, p-COCH₃-Ph, p-COOH-Ph and p-CN-Ph are capable of attracting an electron instead of giving them while p-CH₃-Ph, p-OCH₃-Ph and p-NH₂-Ph are proficient of giving electron rather than capturing which in turn is an indication of their antioxidant ability. BDE is enhanced by substituting the electron withdrawing group at para position while the electron donor group lowers the BDE which would enhance the antioxidant activity. In electron withdrawing substituted derivative, charge density in LUMO is localized on oxygen of hydroxyl due to which abstraction of hydrogen from p-NO₂-Ph, p-COCH₃-Ph, p-COOH-Ph and p-CN-Ph would be difficult. The low IP and BDE value compared to phenol revealed that p-CH₃-Ph, p-OCH₃-Ph, p-NH₂-Ph and p-N(CH₃)₂-Ph would be better antioxidant materials. Finally, antioxidant ability can be improved by substituting the donor group.

Acknowledgements

Authors are thankful to King Khalid University for the support and facilities to carry out the research work.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.arabjc.2013.06.019>.

References

- Aksoy, L., Kolay, E., Agilonu, Y., Aslan, Z., Kargioglu, M., 2013. Saudi J. Biol. Sci. 20, 235–239.
- Antonczak, S., 2008. J. Mol. Struct. THEOCHEM 856, 38–45.
- Aron, P.M., Kennedy, J.A., 2008. Mol. Nutr. Food Res. 52, 79–104.
- Belcastro, M., Marino, T., Russo, N., Toscano, M., 2006. Theor. Chem. Acc. 115, 361–369.
- Chattaraj, P.K., Lee, H., Parr, R.G., 1991. J. Am. Chem. Soc. 113, 1855–1856.
- Frisch, M.J. et al. 2009. Gaussian 09, Revision. Gaussian, Inc., Wallingford, CT.
- Halliwell, B., 2007. Cardiovasc. Res. 73, 341–347.
- Ji, H.F., Tang, G.Y., Zhang, H.Y., 2005. QSAR Comb. Sci. 24, 826–830.
- Kohn, W., Becke, A.D., Parr, R.G., 1996. J. Phys. Chem. 10, 12974–12980.
- Leopoldini, M., Pitarch, I.P., Russo, N., Toscano, M., 2004. J. Phys. Chem. A 108, 92–94.
- Liu, J., Wang, C., Wang, Z., Zhang, C., Lu, S., Liu, J., 2011. Food Chem. 126, 261–269.
- Manach, C., Mazur, A., Scalbert, A., 2005. Curr. Opin. Lipidol. 16, 77–84.
- Mandade, R., Sreenivas, S.A., Choudhury, A., 2011. Free Radic. Antioxid. 1, 87–93.

- Parr, R.G., Pearson, R.G., 1983. *J. Am. Chem. Soc.* 105, 7512–7516.
- Pauling, L., 1960. *The Nature of the Chemical Bond*. Cornell University Press, p. 490.
- Pietta, P.-G., 2000. *J. Nat. Prod.* 63, 1035.
- Rappoport, Z., 2003. *The Chemistry of Phenols Part 2 Patai Series online*. Wiley An Interscience publications, New York.
- Rosane, W.I., Oliveira, Z.D., Fernandes, S.C., Vieira, I.C., 2006. *J. Pharm. Biomed. Anal.* 41, 366–372.
- Stepanic, V., Troselj, K.G., Lucic, B., Markovic, Z., Amic, D., 2013. *Food Chem.* 141, 1562–1570.
- Wright, J.S., Johnson, E.R., DiLabio, G.A., 2001. *J. Am. Chem. Soc.* 123, 1173–1183.
- Xue, Y., Zheng, Y., An, L., Zhang, L., Qian, Y., Yu, D., Gong, X., Liu, Y., 2012. *Comp. Theor. Chem.* 982, 74–83.
- Yamashita, Y., Ouchi, K., 1979. *Carbon* 17, 365.
- Yu, W., Gao, J., Xue, Z., Kou, X., Wang, Y., Zhai, L., 2013. *Food Sci. Hum. Wellness*, <<http://dx.doi.org/10.1016/j.fshw.2013.05.002>> .