SIMULTANEOUS EFFECT OF NITROGEN, TRIFLUOROMETHYL AND DIMETHYLAMINO GROUPS ON THE RADICAL TRAPPING ACTIVITY OF DIPHENYLAMINE: A QUANTUM CHEMICAL STUDY

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Abstract. To maximize the peroxyl radical trapping activity of diphenynlamine, the substituents such as N, NMe_2, and CF_3 are suggested to add to their phenolic rings. The reasonable combination of these substituents at the right position can reduce the bond strength of the N−H bond, but still keep the derivatives stable in air. By substituting N and CF_3 at the *meta* positions and NMe_2 at the *para* positions of both phenolic rings, the bond dissociation enthalpies of N−H calculated at B3P86/6-311G method are around 80.0 kcal/mol but ionization energies calculated at PM6 method are still high enough in the range of 187.9 to 189.0 kcal/mol, resulting in enhancing the radical trapping activity and preventing the one-electron oxidation. Potential energy surface of the reactions between $CH_3OO^{\bullet}$ radical with the selected diphenylamine derivatives was established via the hydrogen atom transfer process.

Keywords: radical trapping antioxidant, bond dissociation enthalpies, ionization energy, potential energy surface, DFT.

Classification numbers: 2.3, 2.3.1.

1. INTRODUCTION

To prevent oils, fuels, plastics, and other chemicals out of autoxidation, enough quantity of chain breaking antioxidants are used with the role of breaking the radical chain reaction by transferring the hydrogen atom to the peroxyl radical in the autoxidation process [1]. As a result, the hydroperoxide and unreactive antioxidant radical will be formed. Industrially, phenols and aromatic amines are promising candidates for this purpose. Especially, diphenylamine

derivatives are considered as radical trapping antioxidants (RTA) and commonly used in the petroleum-derived products [2].

For a given RTA, diphenylamine, for example, the antioxidant and pro-antioxidant reactions always occur at the same time and compete against each other. Both processes of antioxidant and competing pro-antioxidant in rich oxygen were described in Figure 1.

With the effort to enhance the radical trapping activity of the aromatic antioxidants, a strong donating group is usually suggested to be substituted at the *para* position of the aromatic rings [3-6].
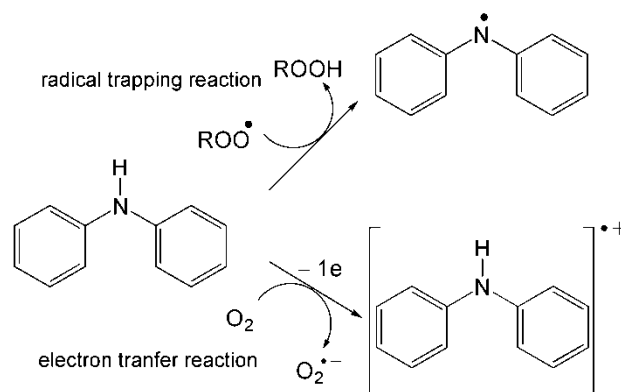

Figure 1. The concurrence of antioxidant and pro-antioxidant reactions in an oxygen-rich environment.
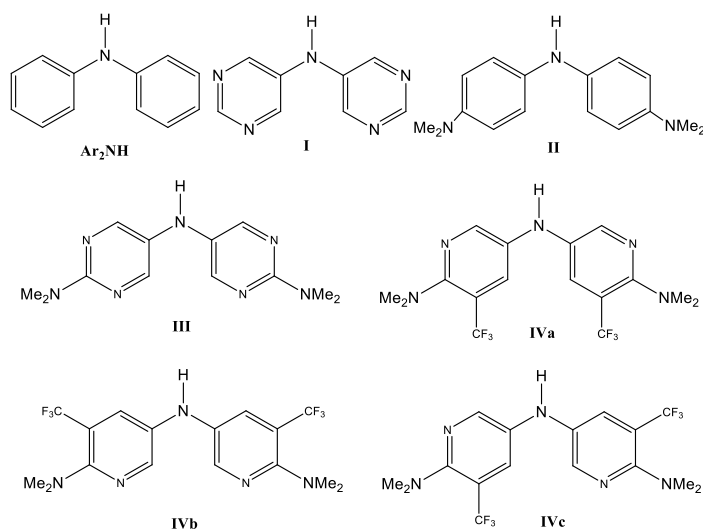

Figure 2. A set of studied diphenylamines.

However, a shortcoming has become from the instability in the air of the derived molecules because of the prooxidant reactions of electron-rich phenolic compounds [4]. Therefore, the topic of an "ideal" radical trapping antioxidant has still abstracted much attention of researchers.

One of the ways to maximize the reactive diphenylamines is to add nitrogens into the rings [3]. Indeed, Valgimigli and coworkers [4] suggested adding nitrogen atoms at the *meta* positions of both phenolic rings and strong donating groups like NMe_2 at the *para* positions. This makes

the diphenylamines become more stable under typical autoxidation conditions (O_2) but still high reactivity in hydrogen donation because of the weakening of the N–H bond.

Based on the available thermo-parameters for substituted diphenylamines [5], we have also found that substituting CF_3 at the *meta* positions of phenolic rings increases slightly the N-H bond dissociation enthalpies (BDEs) but this also increases the ionization energy (IE) considerably, prohibiting the one-electron oxidation. Therefore, if there is a reasonable combination of the substituents at the right positions of the rings, it is also an effective way to enhance the antioxidant activity via the hydrogen abstraction mechanism but still keep them stable in air. Based on the parent diphenylamine (**Ar$_2$NH**), the proposed diphenylamine derivatives consisting N, CF_3, and NMe_2 functional groups were designed and shown in Figure 2. Among them, the compounds **IVa** to **IVc** are similar and the difference is only at the sites of substitution.

With respect to the above-mentioned facts, this study aims to: (1) evaluate the influence of the N, CF_3, and NMe_2 functional groups on the thermochemical properties (BDE and IE) of diphenylamine derivatives; (2) investigate the $CH_3OO•$ radical scavenging activity of potential highly RTA by kinetic calculations.

2. COMPUTATIONAL METHODS

The homolytic BDE(N–H)s and ionization energy (IE) of diphenylamine derivative (YAr$_2$NH) were calculated using the following equations:

$$YAr_2NH \rightarrow YAr_2N^{•} + H^{•} \qquad \text{(BDE)} \qquad (1)$$

$$YAr_2NH - 1e \rightarrow YAr_2NH^{+•} \qquad \text{(IE)} \qquad (2)$$

$$BDE(N–H) = H_f(YAr_2N^{•}) + H_f(H^{•}) - H_f(YAr_2NH) \qquad (3)$$

$$IE = H_f(YAr_2NH^{•+}) - H_f(YAr_2NH) - H(e^-) \qquad (4)$$

where H_f's are the enthalpies at 298.15 K of each species based on the following equation: $H_f = E_0 + ZPE + H_{trans} + H_{rot} + H_{vib} + RT$. In which E_0 is the total energy at 0 K and ZPE is the zero-point vibrational energy. The H_{trans}, H_{rot}, and H_{vib} are the translational, rotational, and vibrational contributions to the enthalpy, respectively.

The enthalpies were calculated at the B3P86/6-311G method for accurate prediction of the BDE(N-H) [7]. In fact, this method has been tested for evaluating BDE(N-H) of a series of diphenylamine, as a result, the difference with the experimental data within 1.0 kcal/mol [7]. And for IE calculations, the PM6 method was applied because it can generate the IE values in good agreement with the experimental data [8].

All computational calculations were carried out using Gaussian 09 program [9]. Rate constants in the gas phase calculated using Eyringpy program [10, 11].

3. RESULTS AND DISCUSSION

3.1. Effect of N, CF$_3$, and NMe$_2$ on the BDE(N-H) and IE of diphenylamines

Hydrogen atom transfer (HAT) and single electron transfer (SET) mechanisms are the main mechanisms for all antioxidants. Based on reactions in Figure 1, the reactivity of the HAT mechanism depends on the BDE of the hydrogen donating bond to the peroxyl radical, and the

latter one is mainly controlled by IE values. Hence, the simultaneous effect of these substituents on BDE and IE should be taken into consideration.

The incorporation of each of the N, CF_3, and NMe_2 substituents into the aryl rings of the diarylamine has changed in both the calculated BDE(N−H) and IE. The calculated BDE(N−H) and IE values for the studied derivatives were given in Table 1, indicating that nitrogen atoms at the 3- and 5-positions of the aryl rings (compound **I**) has a negligible effect on BDE (2.1 kcal/mol), but significant increase in IE value (22.9 kcal/mol). With nitrogen atoms at the 3- and 5-positions and strong electron-donating groups (NMe_2) at the *para* positions (compound **III**) remarkably decrease in BDE (–8.7 kcal/mol) and slightly decrease in IE (–0.5 kcal/mol). The smallest decrease in IE was predicted for compound **II** with NMe_2 on the *para* phenolic rings (–10 kcal/mol), which was accompanied by a significant decrease in the BDE of -8.0 kcal/mol. It is clear that incorporation of N and CF_3 at the *meta* and NMe_2 at the *para* sites strikes the best compromise between maximally increasing the IE while minimally decreasing the N−H BDE. The results suggest that the **IVa**, **IVb** and **IVc** compounds are being known as good RTAs and stable in an oxygen-rich environment.

Table 1. Calculated BDE(N−H) and IE values (in kcal/mol) of the studied compounds.

Compounds	BDE(N−H)[a]	IE[b]
Ar₂NH	87.2	168.6 [165.8][12]
I	89.3 (2.1)	191.5 (22.9)
II	79.2 (–8.0)	158.6 (–10.0)
III	78.5 (–8.7)	168.1 (–0.5)
IVa	80.0 (–7.2)	189.0 (20.4)
IVb	80.6 (–6.6)	188.7 (20.1)
IVc	79.8 (–7.4)	187.9 (19.3)
[a] Using B3P86/6-311G method.		
[b] Using PM6 method.		
- Data in parentheses are the difference between BDE and IE values of the studied compounds compare with one of diphenylamine.		
- Data in parentheses bracket from the references.		

3.2. CH₃OO• radical trapping capability of selected diphenylamines

In this part, to better understand the H donation process, the potential energy surface (PES) was calculated for the reaction between $CH_3OO^\bullet$ radical with the diphenylamine (Ar_2NH) and the compound **IVc** at the M05-2X/6-311++G(d,p) method that has been highly recommended for kinetic calculations [13]. Rate constants for hydrogen atom transfer processes at the N-H bond were also computed at the same level of theory using the conventional transition state theory (TST). As shown in Figure 3, each reaction has two intermediates (pre-reactant complex - RC and product complex - PC) and one transition state (TS) of transferring H atom to $CH_3OO^\bullet$. Based on these PES's, it is found that the barrier energy of TS-**IVc** (7.9 kcal/mol) is lower than one of TS–Ar_2NH (11.9 kcal/mol), in a good

agreement with the trend of the BDE value in the thermodynamic study. Therefore, the process of transferring H to $CH_3OO^\bullet$ of compound **IVc** is easier than that in the parent diphenylamine. Analyzing the data from Table 2 shows that the reaction of $CH_3OO^\bullet$ with the compound **IVc** is favorable due to the lower activation Gibbs free energies at 12.7 kcal/mol and the almost negative values of Gibbs energies (−3.2 kcal/mol). Comparing with the typical antioxidant butylated hydroxytoluene –BHT ($k = 1.51$ x 10^4 $M^{-1}s^{-1}$), the $CH_3OO^\bullet$ scavenging rate of **IVc** ($k = 9.63$ x 10^4 $M^{-1}s^{-1}$) is nearly 6 times higher. Therefore, compound **IVc** is considered as a potential antioxidant used in the petroleum-derived products.

Table 2. Activation ($\Delta G^{\neq}$), reaction (ΔG) Gibbs free energies and rate constants (k) calculated at the M05-2X/6-311++G(d,p) level of theory at 298.15 K in the gas phase.

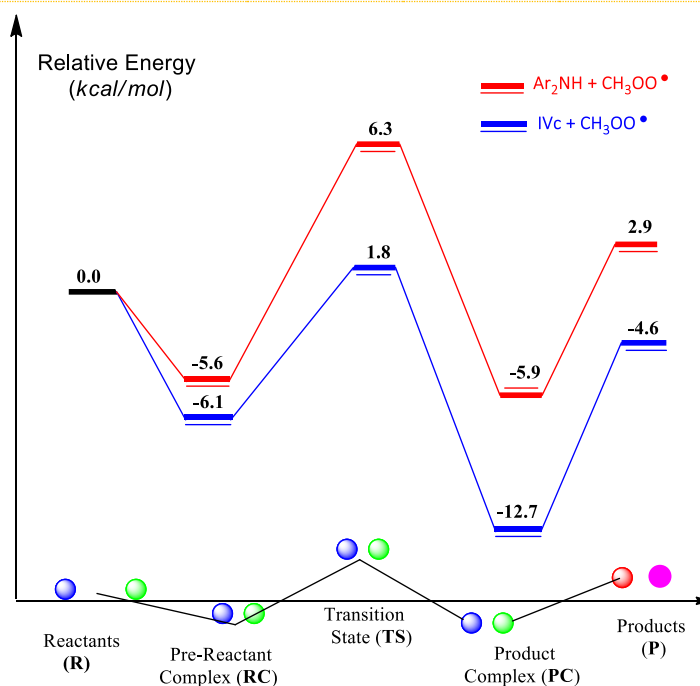| Reactions	ΔG (kcal/mol)	$\Delta G^{\neq}$ (kcal/mol)	k $M^{-1}s^{-1}$
$Ar_2NH + CH_3OO^\bullet$	4.0	16.9	1.38×10^3
$IVc + CH_3OO^\bullet$	−3.2	12.7	9.63×10^4
$BHT + CH_3OO^\bullet$	−5.3	14.5	1.51×10^4

Figure 3. The PES of compounds (Ar_2NH) and (**IVc**) with $CH_3OO^\bullet$ radical.

4. CONCLUSIONS

The effect of N, CF_3, and NMe_2 on the BDE and IE of diphenylamine has been examined using the B3P86/6-311G and PM6 methods. By adding N and CF_3 at the *meta* and NMe_2 at the *para* sites of both aromatic rings, we established the novel compounds that are much more stable to electron-transfer reactions to O_2 due to higher inherent IEs, but which remain highly reactive

to hydro atom transfer reactions since they still possess relatively low N−H BDEs. This substitution also causes the reaction between these studied compounds to be more favored via the HAT mechanism. Among the studied compounds, **IVc** is one of the most potential antioxidants, with the rate constants is 9.63 x 10^4 $M^{-1}s^{-1}$ in the gas phase.

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