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# DFT studies of the effectiveness of *p*-phenylenediamine antioxidants through their Cu(II) coordination ability

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ABSTRACT

In B3LYP optimized structures of $Cu^{2+}$ complexes with a series of *p*-phenylenediamine (PPD) antioxidants the copper atom prefers bonding to the nitrogen atom between aromatic rings ($N_1$ site). The PPD antioxidant effectiveness rises with increasing PPD affinity to $Cu^{2+}$ ions, decreasing charges and spin densities at Cu atoms and the increasing electron density transfer in Cu–N bonds in the $^2[PPD\cdots Cu]^{2+}$ complexes with copper atoms bonded at $N_1$ site unlike remaining N sites. Cu bonding to tertiary carbon atoms is excluded due to the absence of frontier molecular orbitals density at these atoms in PPD molecules.

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## 1. Introduction

The rate of the oxidative degradation of organic materials which are exposed to oxygen can be reduced using antioxidants (Aox). Aromatic secondary amines, particularly *N*-phenyl-*N′*-alkyl-*p*-phenylenediamines (PPD) are the most important commercial antioxidants used prevailingly in rubber industry [1,2]. The most important reactive radical intermediates formed during degradative reactions are hydroxyl (HO•), alkoxyl (RO•) and peroxyl (ROO•) radicals which can readily abstract hydrogen atoms from polymer molecular backbones, ultimately breaking down the polymer molecules. The supposed mechanism of inhibition by phenylenediamines consists of several steps. Reaction products of primarily formed amine radicals are benzoquinonediimines and nitroxyl radicals, which have antioxidative effects as well (the benzoquinonediimines due to the subsequent regeneration of nitroxyl trapping species). The benzoquinonediimine-type products may finally undergo hydrolytic or condensation reactions by forming benzoquinonemonoimine-type structures or N-heterocyclic compounds [1,2].

Simon et al. investigated the relation between the structure of the PPD antioxidants and their efficiency in polyisoprene rubber (PIR) by non-isothermal DSC (Differential Scanning Calorimetry) measurements [3–11]. Free radicals concentration during the induction period determines the rate of the oxidation reaction which can be reduced using antioxidants. The antioxidant activity can be evaluated as the ratio of the lengths of the induction periods $t_i$ of the stabilized (PIR+AOx) and unstabilized (PIR) polymer since the stability or non-stability of the polymer is brought about the same structural units both in stabilized and unstabilized polymer. The protection factor, *PF*, is defined as

$$PF = \frac{t_{\mathrm{i}}(\mathrm{PIR} + \mathrm{AOx})}{t_{\mathrm{i}}(\mathrm{PIR})} \tag{1}$$

The greater is the value of *PF*, the higher is the antioxidant effectiveness of the additive. The values of protection factors decrease with increasing temperature and decreasing concentration of the antioxidant. As the dependence of the protection factor on the antioxidant concentration is almost linear, the Molar Antioxidant Effectiveness (*AEM*) can be defined as

$$AEM = \frac{PF - 1}{m} \tag{2}$$

where $m$ is the concentration of antioxidant in polymer matrix expressed in mol $kg^{-1}$.

Simon et al. [3–11] have found that the effectiveness of a series of antioxidants under study is indirectly proportional to the dissociation energy of the C–H bond at the tertiary carbon atom in the neighbourhood of the nitrogen atom. Substitution of all hydrogen atoms at this carbon atom leads to a loss of antioxidant

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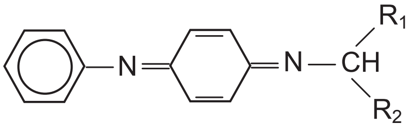
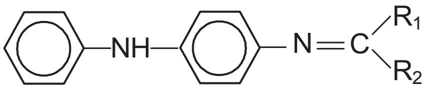
**Table 1**
Studied antioxidants notation and their Molar Antioxidant Effectiveness (AEM) at 130 °C [3–11].

| Acronym | Compound name | AEM [kg/mol] |
|---|---|---|
| DPPD | *N,N′*-diphenyl-*p*-phenylenediamine | 738 |
| SPPD | *N*-phenyl-*N′*-(1′-methylbenzyl)-*p*-phenylenediamine | 351 |
| 6PPD | *N*-phenyl-*N′*-(1,3-dimethyl-butyl)-*p*-phenylenediamine | 277 |
| IPPD | *N*-phenyl-*N′*-isopropyl-*p*-phenylenediamine | 177 |

properties. This fact leads to a justifiable assumption that, in the mechanism of antioxidation effect of PPDs, instead of the classical benzoquinonediimine-type structure



the ketimine molecule should be included:



where $R_1$ and $R_2$ are substituents.

In order to find the relation between the structures of PPD antioxidants and their *AEM* values some of them were investigated theoretically by Density Functional Theory (DFT) model studies as well [5,6,8,12–15]. PPD structures in the protected materials significantly depend on solid state effects and so it is very problematic to find suitable characteristics of the PPD molecules with the least possible dependency on their conformations. In our recent

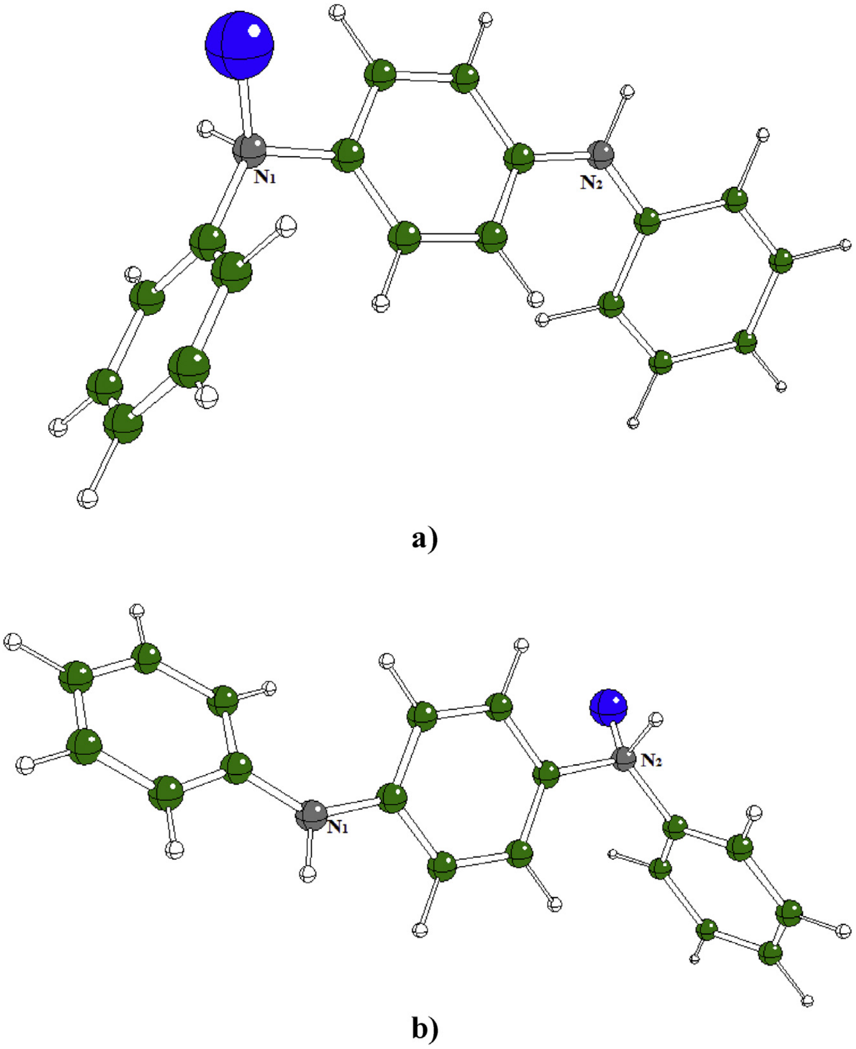


**Fig. 1.** Optimized structure of $^2[\mathrm{DPPD}\cdots\mathrm{Cu}]^{2+}$ with Cu atom a) at $N_1$ site and b) at $N_2$ site (Cu – blue, N – gray, C – green, H – white). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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