

ON THE ANTIOXIDANT EFFECTIVENESS OF N,N'-SUBSTITUTED P-PHENYLENEDIAMINES

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Received 16 August 2004; received in revised form 18 October 2004; accepted 28 October 2004

Abstract

The ground-state geometry of six N,N'-substituted p-phenylenediamines (PPDs): N-phenyl-N'-dimethyl-butyl-p-phenylenediamine (6PPD), N-phenyl-N'-isopropyl-p-phenylenediamine (IPPD), N-phenyl-N'-(α -methylbenzyl)-p-phenylenediamine (SPPD), N-(2-methoxybenzyl)-N'-phenyl-p-phenylenediamine (MBPPD), N-benzyl-N'-phenyl-p-phenylenediamine (MBPPDH), N-(1-methyl-1-phenylethyl)-N'-phenyl-p-phenylenediamine (CPPD) molecules, their radical structures and the energy characterisation of these molecules and radicals were theoretically investigated using PM3 method. Our calculations reveal the most probable radical formation in the order SPPD > MBPPD > MBPPDH > 6PPD > IPPD > CPPD. The theoretical values have been compared with the values obtained by the analysis of structural units contributions based on the results of non-isothermal DSC measurements. The results show that the most likely process is homolytic cleavage of C-H bond at the carbon atom in the neighbourhood of the amino nitrogen atom and the sterical arrangement is related to the antioxidant effectiveness of the antioxidants under study. The suggested models can be used for the interpretation and prediction of experimental data what is important from the technological point of view.

Key words: Quantum chemical calculations, PM3, antioxidants, antioxidant effectiveness, p-phenylene diamines

Introduction

Technical and economic problems arising from negative influence of the environment on polymer durability have been studied since the commercial introduction of polymers. Polymer lifetime is controlled by both oxidation and mechanical degradation, mostly proceeding independently [1]. Oxidation reactions are enhanced especially at elevated temperatures during the processing of the polymer [2, 3, 4]. However, they may

become important already at relatively low temperatures. Thermal oxidation of thermoplastics and elastomers may occur during every stage of their life cycle. It can take place already during the polymerization, following processing, and on storage. The rate of thermal degradation is pronounced during the polymer treatment. Thermal degradation during the lifetime of the plastics depends mainly on the enviro-

nmental conditions [4]. The main consequence of thermal oxidation is the loss of mechanical properties of polymers.

Thermal oxidation of polymers generally corresponds to a free radical chain reaction [4, 5, 6]. It involves initiation reactions generating free radicals, propagation reactions yielding hydroperoxides, and termination reactions eliminating free radicals from the system. Initiating polymer radicals are formed through the action of heat or the combination of heat and mechanical stress (especially under processing conditions). The radicals formed in the initiation, propagation, and chain branching steps are not only able to fix oxygen and/or abstract hydrogen. They may be subject to unimolecular decomposition reactions, too. These reactions lead to chain scissions, i.e. to a decrease in polymer molecular weight. On the other hand, bimolecular termination reactions give rise to crosslinking and an increase in polymer molecular weight.

Substances reducing or inhibiting thermal oxidation are called antioxidants. Antioxidants may intervene in any step in the thermal oxidation. They can be divided into two general groups: primary antioxidants, which act as free-radical scavengers to interrupt or prevent oxidation reactions; and secondary antioxidants, which react with hydroperoxide groups (their formation is a stage in the oxidation reaction chain) to convert them to non-radical products [4, 7, 8].

The primary antioxidants are typically compounds containing sterically hindered phenolic OH groups, secondary aromatic amines, and sterically hindered amines (HAS). HAS are usually employed as light stabilizers and, indeed, they are often referred to as hindered amine light stabilizers (HALS). Primary antioxidants can be used for prestabilization and long-term stabilization of the polymers [4, 8].

The secondary antioxidant group consists of phosphites, phosphonites, thioesters, and metal salts. They are used in combination with primary antioxidants during processing and for long-time stabilization under severe thermal conditions [4].

Secondary aromatic amines and diamines are antidegradants with a long history of use. They are discoloring and staining and therefore are not generally suitable for use in plastics. Their application has been mostly restricted for carbon black-filled vulcanized rubbers.

Phenylenediamines are considered to function as a chain breaking antioxidants (via hydrogen donation) forming aminyl radicals. The mechanism of inhibition by the *p*-phenylenediamines (PPDs) is given in Scheme 1. Benzoquinonediimines (BQDI) were isolated as reaction products of the first step. As can be seen from Scheme 1, their chemistry involves condensation, hydrolytic and redox reactions. Compounds with benzoquinonemonoimine (BQMI) structures and *N*-heterocyclic compounds are formed and the structure of substituted phenylenediamines is regenerated. BQDI are able to trap R[•] radicals. This contributes to the antioxidant efficiency of the originally added phenylenediamine derivative due to the regeneration of the RO₂ trapping species [9].

The antioxidant activity of six PPDs (CPPD, DPPD, IPPD, MBPPD, SPPD and 6PPD, see Figure 1) in polyisoprene rubber has been experimentally studied by differential scanning calorimetry (DSC) under non-isothermal conditions. A new criterion characterizing the antioxidant effectiveness, *AEM*, as a slope of the concentration dependence of the protection factor has been proposed [10]. Using this criterion, the effectiveness of antioxidants under study was in the order DPPD > SPPD > 6PPD > IPPD > MBPPD > CPPD.

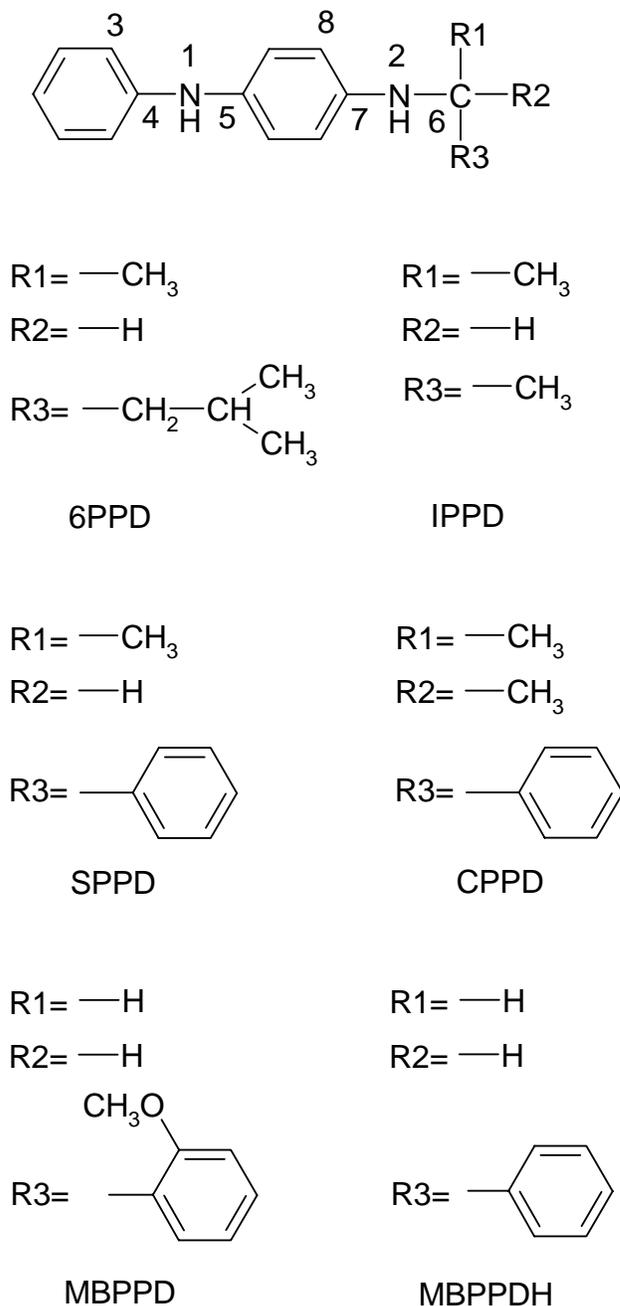


Figure 1. Notation of the compounds under study.

The action of PPDs was experimentally studied also by other authors [11–13] and reaction products were identified. On the other hand, no theoretical works dealing with structural and energy characterization of these antioxidants and radicals derived from them are available. With respect to the data available from literature, the aim of this study is a deeper insight into the mechanism

and energetics of the antioxidant effectiveness of the ground-state geometry of six *N,N'*-substituted *p*-phenylenediamines (PPDs): *N*-phenyl-*N*-dimethyl-*p*-phenylenediamine (6PPD), *N*-phenyl-*N*-isopropyl-*p*-phenylenediamine (IPPD), *N*-phenyl-*N*-(α -methylbenzyl)-*p*-phenylenediamine (SPPD), *N*-(2-methoxybenzyl)-*N*-phenyl-*p*-phenylenediamine (MBPPD), *N*-

benzyl-*N*-phenyl-*p*-phenylenediamine (MBPPDH), *N*-(1-methyl-1-phenylethyl)-*N*-phenyl-*p*-phenylenediamine (CPPD) molecules and their radical structures and the relevant energetical characterisation of the inhibition scheme using the PM3 quantum chemical calculation method [14].

The optimal geometry of the most stable conformers will be investigated and the heat of radical formation will be presented. Obtained results may be useful for the

Results and discussion

At the beginning, the conformational analysis has been carried out for the studied compounds and their radicals on N(1), N(2), C(6) and N(1)N(2) biradicals after corresponding hydrogen atoms splitting-off. In our study we have restricted our attention to the most stable conformations because the differences between various conformations in interatomic distances are practically negligible. Benzene ring with the two nitrogen atoms is planar in ground state. Values of the torsional angles $\alpha(3-4-1-5)$ and $\beta(8-7-2-6)$ are in the range 120–130° and 36–45°, respectively. All studied antioxidant molecules have very similar volume to surface area ratios 1.62–1.68 $\times 10^{-10}$ m (calculated using QSAR approach [16]). This parameter can be in direct relation to the diffusion process. The antioxidants with large volumes have decreased mobility in polymer matrix and their diffusion to polymer surface may be restricted. It has been demonstrated, that the rate of diffusion of additives decreases with increasing molecular weight of the additive [1].

Preparation of new materials for technological applications requires good intuition on the possible mechanisms that determine the oxidation processes in polymers. Information contained in many-electron wave functions is too complex and thus it is very unlikely to get physical insight into the structure-function relationship for an additive in this way. The calculated values of heat of reactions offer a reasonable compromise from the energy point of view. In this work we have calculated heat of

choice of suitable candidates for possible technological applications.

Quantum Chemical Methods

The ground-state geometry of studied molecules were optimized at the Hartree-Fock level using the standard semiempirical PM3 method [14] of the Hyperchem program package [15] (energy cut-off of 10^{-5} kJ·mol⁻¹, final RMS energy gradient under 0.01 kJ·mol⁻¹ Å⁻¹).

reaction values for four different radicals: $\Delta_r H_1$ for radical formation on N(1) atom, $\Delta_r H_2$ for radical formation on N(2), $\Delta_r H_3$ for biradical formation on N(1) and N(2), and $\Delta_r H_4$ for radical formation on C(6) atom. Table 1 summarizes all energy values calculated within PM3 approach for studied molecules and their radicals. These indicate, that most probable radical formation process is C(6)–H bond splitting-off, because it has the lowest energy requirement. Therefore we can conclude that this process is the most important in antioxidant action of these antioxidants. We can support this assumption by the fact, that CPPD which has not any hydrogen atom on C(6) shows no antioxidant action [10]. Radical formation on N(1) is energetically favoured against the radical on N(2). Energy demand for biradical formation ($\Delta_r H_3$) is almost the same as the sum of reaction heat values of radical formation on N(1) and N(2), i.e. $\Delta_r H_1 + \Delta_r H_2$. It indicates that radical formation on one nitrogen atom does not significantly affect the radical formation on the other.

Since studied antioxidants consist of several repeating structural units, we tried to analyze contributions of these units to the antioxidant activity. This approach is based on the assumption, that overall activity of the antioxidant may be calculated as the total of the contributions of the structural units in the molecule. Calculated values (Table 2) are relative to the “molecular skeleton” (I, see Fig. 2). In the calculation we used the model

Table 1 Calculated PM3 heat of formations H_f ; partial charges on N(1), N(2), and C(6); reaction heat values of various radical formation.

Molecule	Ground state (G)				N(1) Radical	N(2) Radical	N(1)N(2)) Biradical	C(6) Radical
	H_f (kJ·mol ⁻¹)	$q_{N,1}$	$q_{N,2}$	q_C	$\Delta_r H_1$ (kJ·mol ⁻¹)	$\Delta_r H_2$ (kJ·mol ⁻¹)	$\Delta_r H_3$ (kJ·mol ⁻¹)	$\Delta_r H_4$ (kJ·mol ⁻¹)
SPPD	302.410	-0.002	0.107	-0.014	131.515	136.745	293.185	82.200
6PPD	81.113	0.030	0.110	-0.080	141.460	149.912	306.787	111.878
IPPD	146.350	0.032	0.110	-0.080	141.150	149.381	306.716	116.313
MBPPD	167.706	0.021	0.110	-0.046	138.600	142.404	297.257	96.520
MBPPDH	313.768	0.036	0.113	-0.052	138.617	145.602	297.252	96.545
CPPD	276.365	0.016	0.111	0.028	142.751	154.568	309.696	-

Note: $H_f(H) = -0.042$ kJ mol⁻¹

Table 2 Contribution of molecular fragments to antioxidant activity (values are relative to "molecular skeleton" I).*

Fragment	Contribution to AEM
C(II)	-1 128
H(III)	546
CH ₃ (IV)	195
CH ₂ (V)	-586
CH(VI)	491
Phenyl (VII)	369

* Denotations of fragment are shown in Fig. 2

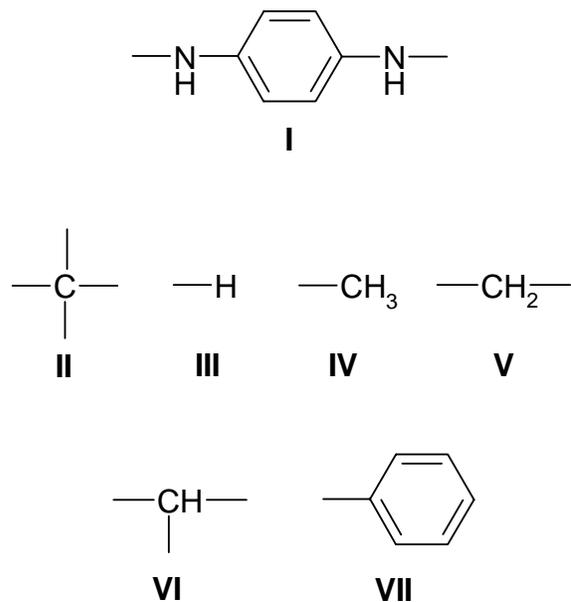
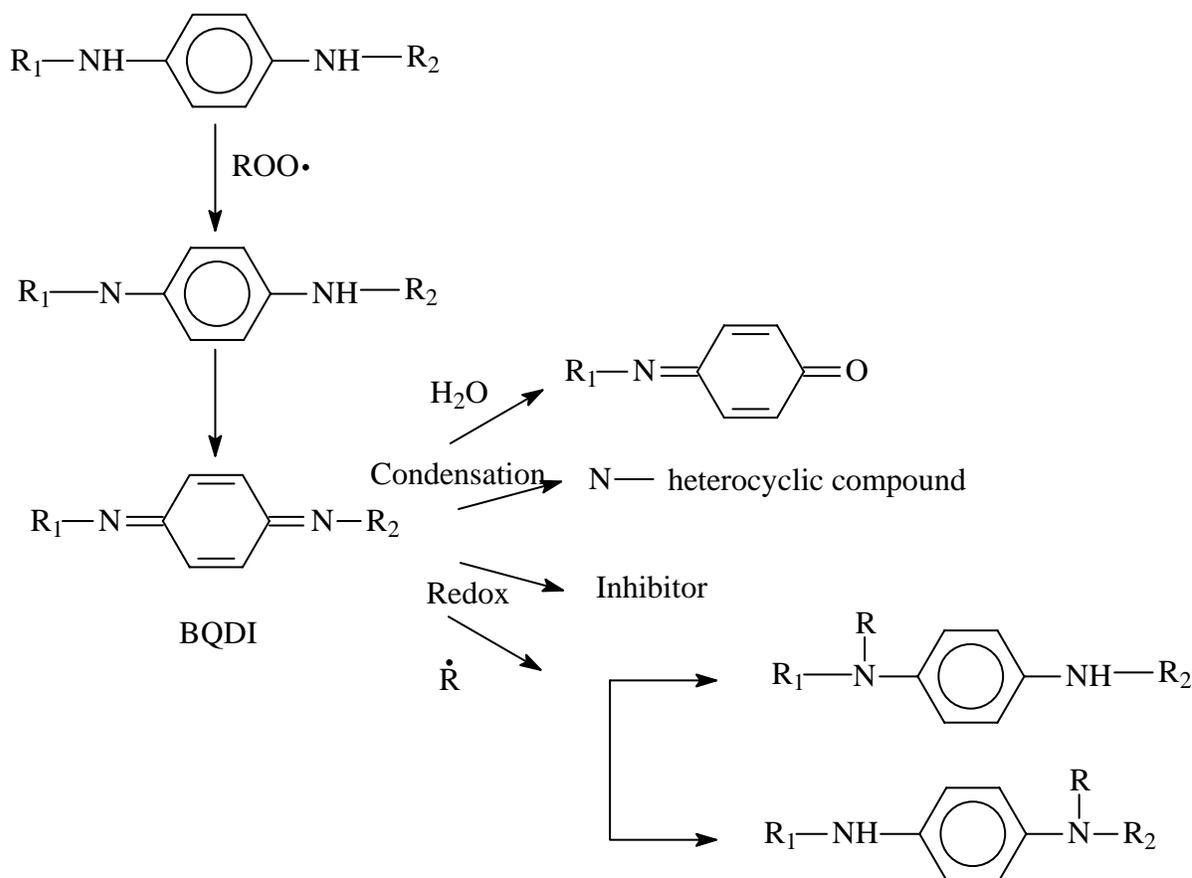


Figure 2. Structural units of studied antioxidants.



Scheme 1. The mechanism of inhibition effect of PPDs.

MBPPDH molecule instead of MBPPD molecule. Neglecting the CH_3O- group presence has allowed the calculation of structural unit contributions. We anticipate that this group does not have any significant influence on the antioxidant activity of the MBPPD. This is confirmed also by the results of PM3 method, where all reaction heat values of the two molecules are almost identical. Therefore we suppose that AEM value obtained for MBPPD can be used for MBPPDH, too. The results confirm important role of hydrogen (III) on C(6) carbon that we have already proven by quantum chemical calculations. Phenyl and CH (fragments VII and VI) contribute to antioxidant activity positively, too. On the other hand, this calculation shows very strong negative effect of the carbon II. When more antioxidants of similar structure will be

synthesized and their effect will be tested, we plan to compare obtained experimental results with the results of this analysis. We expect that presented concept of structural unit contributions may be applied for the approximate prediction of antioxidant effect of new substances.

Conclusion

In this article, a systematic study of six *N,N'*-substituted *p*-phenylenediamines molecules with antioxidant effects is presented (see Figure 1). The optimal geometries of these structures and their radical forms occurring in inhibition scheme were obtained by semiempirical quantum-chemical PM3 method. Our calculations reveal the most probable radical formation in the order $SPPD > MBPPD > MBPPDH > 6PPD >$

IPPD > CPPD. The comparison of the theoretical results and analysis of the structural units contributions based on results of the non-isothermal DSC measurements shows that the ability of radicalisation of C–H bond in the neighborhood of amine group and the sterical arrangement are directly proportional to the antioxidant effectiveness of the antioxidants under study.

It can be concluded that this type of antioxidants represents a perspective basis for material research in polymer science and industry. In order to understand the inhibition mechanism and to predict the antioxidant effectiveness of PPDs the suggested models should be applied for much more similar structures.

Acknowledgements

This work has been supported by Slovak Grant Agency (Projects No. 1/0054/03, and 1/0055/03)

References

- [1] White J. R., Rapoport N. Y.: *Trends Polym. Sci.*, **1994**, 2, 197.
- [2] Kim T. H., Oh D. R.: *Polym. Degrad. Stab.*, **2004**, 84, 499.
- [3] Pospíšil J., Habicher W.-D., Pilař J., S. Nešpůrek, Kuthan J., Piringer G.-O., Zweifel H.: *Polym. Degrad. Stab.*, **2002**, 77, 531.
- [4] Gugumus F.: *Oxidation Inhibition in Organic Materials*, Vol. 1, CRC Press 1990, Boca Raton.
- [5] Bolland J. L. and Gee G.: *Trans. Faraday Soc.*, **1946**, 42, 236.
- [6] Bolland J. L.: *Trans. Faraday Soc.*, **1948**, 44, 669.
- [7] Titow W. V.: *PVC PLASTICS Properties, Processing and Applications*, Elsevier Publishers 1990, New York.
- [8] Wolf R., Kaul B. L.: *Ullmann's Encyclopedia of Industrial Chemistry*, **1992**, A20, 461.
- [9] Pospíšil J., Klemchuk O. P.: *Oxidation Inhibition in Organic Materials*, Vol. 1, CRC Press, 1990.
- [10] Cibulková Z., Šimon P., Lehocký P., Balko J.: *submitted to the Polym. Degrad. Stab.* **2004**
- [11] Cataldo F.: *Polym. Degrad. Stab.*, **2001**, 73, 511 and references therein.
- [12] Cataldo F., Heymann D.: *Polym. Degrad. Stab.*, **2000**, 70, 237.
- [13] Stenberg B., Shur J., Jansson J. F.: *J. Appl. Polym. Sc. Appl. Polym. Symp.*, **1979**, 35, 311.
- [14] Dewar M.J.S., Zoebisch E.G., Healy E.F., Stewart J.J.P.: *J. Am. Chem. Soc.* **1985**, 107, 3902.
- [15] *HYPERCHEM, rel. 3 for Windows*, Hypercube, Inc. **1993**.
- [16] Borman S.: *Chem. Eng. News*, **1990**, 68, 20.