

ON THE ENERGETICS AND TORSIONAL EFFECTS OF SELECTED *N,N*-SUBSTITUTED *p*-PHENYLENEDIAMINES

V. Lukeš¹ and Z. Cibulková²

¹Department of Chemical Physics, Slovak University of Technology, Radlinského 9, SK-812 37 Bratislava, Slovak Republic, e-mail: vladimir.lukes@stuba.sk

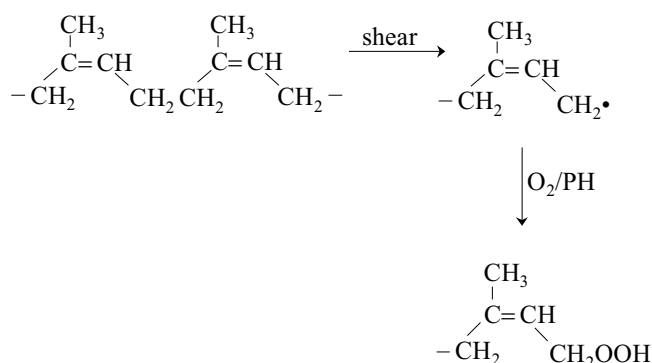
²Department of Physical Chemistry, Slovak University of Technology, Radlinského 9, SK-812 37 Bratislava, Slovak Republic, e-mail: zcibulka@lycos.com

Abstract. The following *p*-phenylenediamines (PPD): *N,N*-diphenyl-*p*-phenylenediamine (DPPD), *N*-phenyl-*N*-(2-phenyl-ethyl)-*p*-phenylenediamine (SPPD) and *N*-isopropyl-*N*-(phenyl)-*p*-phenylenediamine (IPPD) have been theoretically studied using the semiempirical quantum chemistry methods. The ground-state geometry of selected molecules and intermediates and the relevant energetical characterisation of the inhibition reaction scheme were investigated using AM1 method. The electron absorption spectra for stable conformers were obtained by ZINDO/S method. Finally, the molecular dynamics simulation using MM+ method at constant temperature ($T = 350\text{K}$) was used to determine the torsional oscillations near the active nitrogen atom. The obtained theoretical results agree with the available experimental data.

Key words: electron absorption spectra, Antioxidant, Polyisoprene, DPPD, IPPD, SPPD.

Introduction

Polyisoprene (PI) rubber is widely used in many applications. Rubber products have to withstand a wide range of conditions during service. For example, rubber products are subjected to the effects of high temperatures in the presence of significant concentrations of oxygen. Unfortunately, the reaction of rubber with atmospheric oxygen causes a degradation of the mechanical and chemical properties of PI rubber. The thermal oxidation of PI is an autocatalytic, free radical chain reaction with oxygen, with oxidation products being oxygenated groups such as ketones, aldehydes, carboxylic acids, etc. The degradation process starts with the formation of free radicals during the induction period (Scheme 1) [1] and the concentration of free radicals determines the rate of the oxidation

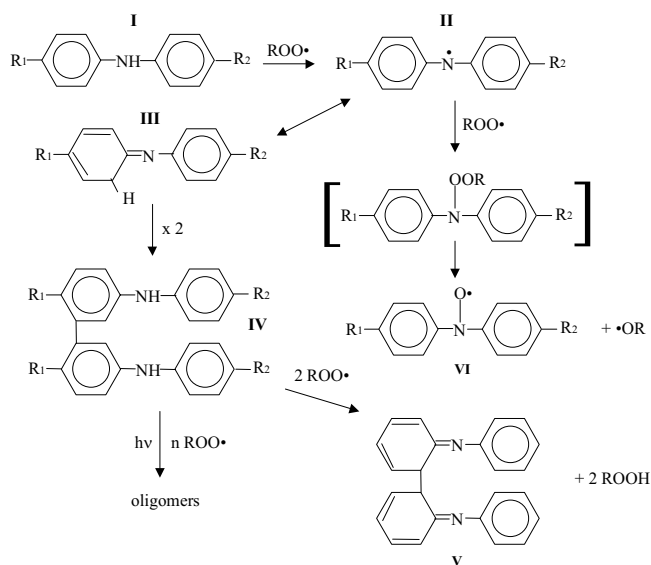


Scheme 1. Formation of free radicals during the induction period.

when sufficient amount of oxygen is present. The rate of oxidation reaction can be reduced using antioxidants. The antioxidants decrease the concentration of free radicals available to react with PI rubber by the preferential reaction with the free

radicals formed during the induction period. *N,N*-substituted *p*-phenylenediamines (PPDs), for example, *N,N*-diaryl-*p*-phenylenediamine (DPPD), *N*-phenyl,1-phenyl-*N*-(ethyl)-*p*-phenylenediamine (SPPD) and *N*-isopropyl,1-phenyl-*p*-phenylenediamine (IPPD) are most widely used antioxidants for PI rubber [2-4]. These have the ability to inhibit thermal oxidation and ozone degradation. The mechanism of inhibition effect of PPDs is given in Scheme 2 [5]. The first step is the formation of amine radical II, which is highly reactive. It is converted rapidly either to oligomers of the compound III or to nitroxyl radicals VI. Products of these reactions are even more effective antioxidants than the parent amines [1,5].

The mechanism of antioxidant protection of PPDs was experimentally studied by several authors [8-12]. The antioxidant activities of selected PPDs were determined also using differ-



Scheme 2. Inhibition mechanism of substituted diphenylamines.

ential scanning calorimetry (DSC) [11,12]. On the other hand, no theoretical works dealing with structural and energetical characterization of the intermediates and products occurring during the inhibition of PI rubber oxidation are available. With respect to this fact, the aim of this study is a deeper insight into the mechanism and energetics of the antioxidant effects of DPPD, IPPD and SPPD using the AM1 quantum chemical calculation method [13]. The theoretical electron absorption spectra will be calculated using the ZINDO/S method [14]. Finally, the molecular dynamics simulation using MM+ method [15] at constant temperature ($T = 350\text{K}$) will be used to determine the torsional oscillations near the active nitrogen atom. All these information may be useful for the choice of suitable candidates for possible technological applications.

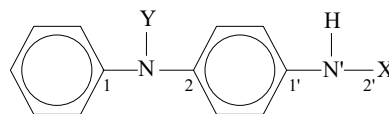
Quantum Chemical Methods

The ground-state geometry of selected molecules (see Figure 1) were optimised (at the Hartree-Fock level) using the standard semiempirical AM1 (Austin Model 1) method [16,17] of the MOPAC 7.0 package [18] (energy cut-off of $10^{-5} \text{kJ}\cdot\text{mol}^{-1}$, final RMS energy gradient under $0.01 \text{kJ}\cdot\text{mol}^{-1} \text{\AA}^{-1}$). On the basis of the optimised geometries, the electronic spectra were calculated by standard semiempirical ZINDO/S method for single excitations from 5 highest occupied to 5 lowest unoccupied molecular orbitals at the single level of theory using σ - σ and π - π overlap weighting factors of 1.30 and 0.55, respectively [14,19]. The time dependence of the selected torsional motions (Θ_1 between 2-N-3-4 atoms and Θ_2 between 1-2-N-3 atoms) for thermal equilibrium at $T = 350 \text{K}$ was calculated using MM+ level of theory [15]. The run time was set to the 0.1 ps value and the scan was realised with 0.0005 ps step.

Results and Discussion

The structure of compounds and intermediates under study (see Figure 1) may be briefly characterised by angles α (1-N-2) and β (1'-N'-2') and bond lengths between the nitrogen atoms and their neighbours (see Table 1). Our study was re-

stricted to the most stable conformations because the differences in interatomic distances and/or optical properties are practically negligible.



Molecule	-X	-Y
DPPD	-C ₆ H ₅	-H
DPPD·	-C ₆ H ₅	-
DPPD-OOR	-C ₆ H ₅	-OOR
DPPD-O·	-C ₆ H ₅	-O·
IPPD	-CH(CH ₃)- CH ₃	-H
IPPD·	-CH(CH ₃)- CH ₃	-
IPPD-OOR	-CH(CH ₃)- CH ₃	-OOR
IPPD-O·	-CH(CH ₃)- CH ₃	-O·
SPPD	-CH(CH ₃)- C ₆ H ₅	-H
SPPD·	-CH(CH ₃)- C ₆ H ₅	-
SPPD-OOR	-CH(CH ₃)- C ₆ H ₅	-OOR
SPPD-O·	-CH(CH ₃)- C ₆ H ₅	-O·

Figure 1. Notation of the compounds under study.

Radicalisation of the nitrogen atoms leads to a shortening of the interatomic distances (1-N and N-2) of about -0.04\AA . This may be explained by a lower repulsion due to the lowering (about twice) of the negative charge on the active nitrogen atom. On the other hand, the presence of the oxygen atom on the nitrogen atom has the opposite effect, the bonds are prolonged ($+0.04 \text{\AA}$). On the basis of the optimised AM1 geometry, the volume and surface of the molecule were calculated. The ratios of these quantities using QVASR approach [20] increase from DPPD ($831 \text{\AA}^3/813 \text{\AA}^2$), SPPD ($918 \text{\AA}^3/559 \text{\AA}^2$) to the IPPD ($769 \text{\AA}^3/477 \text{\AA}^2$). In Table 1, we present also the ionisation potentials (IP) of the studied antioxidants. The value of 7.8 or 7.9 eV is typical for most organic molecules and reveals no special trends.

Table 1. The calculated heat of formations (ΔH_f), ionisation potentials (IP), relative charges on nitrogens and selected geometrical parameters (see Fig. 1)

Molecule	ΔH_f (kJ/mol)	IP (eV)	Charge N	Bond length (\AA)			Angle ($^\circ$) 1-N-2	Charge N'	Bond length (\AA)			Angle ($^\circ$) 1'-N'-2'
				1-N	N-2	1-N-2			1'-N'	N'-2'	1'-N'-2'	
DPPD	380.55	-7.9	-0.25	1.41	1.41	122	-0.25	1.41	1.41	122		
DPPD·	459.76	-	-0.12	1.37	1.36	122	-0.26	1.39	1.40	124		
DPPD-OOR	516.44	-	-	-	-	-	-	-	-	-		
DPPD-O·	430.54	-	0.14	1.44	1.43	121	-0.26	1.40	1.41	123		
IPPD	202.14	-7.8	-0.25	1.41	1.41	121	-0.27	1.41	1.46	119		
IPPD·	281.15	-	-0.11	1.37	1.36	122	-0.27	1.40	1.45	121		
IPPD-OOR	303.05	-	-	-	-	-	-	-	-	-		
IPPD-O·	250.09	-	0.14	1.44	1.43	121	-0.27	1.40	1.45	121		
SPPD	357.56	-7.8	-0.24	1.41	1.41	119	-0.27	1.41	1.46	122		
SPPD·	436.35	-	-0.11	1.37	1.36	124	-0.27	1.40	1.46	126		
SPPD-OOR	497.75	-	-	-	-	-	-	-	-	-		
SPPD-O·	409.60	-	0.13	1.44	1.43	121	-0.28	1.40	4.46	123		

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 unlikely to provide physical insight into the structure-function relationship. The calculated values of heat of formations offer a reasonable compromise from the energetical point of view. Table 1 collects the ΔH_f values calculated within AM1 approach for selected molecules. As can be seen, the extraction of the hydrogen atom from the nitrogen bridge leads to comparable differences of H_f values (79.21 kJ.mol⁻¹ for DPPD, 79.00 kJ.mol⁻¹ for IPPD and 78.79 kJ.mol⁻¹ for SPPD). The ability of the radical formation is slightly lower for the DPPD. The energetical barriers for the studied reaction path increases from IPPD (92.80 kJ.mol⁻¹), DPPD (127.49 kJ.mol⁻¹) to SPPD (132.51 kJ.mol⁻¹). Energetically, IPPD system differs from DPPD and SPPD ones.

A better view on the thermal stability as well as the torsional oscillations of two angles near the active nitrogen atom is offered by the molecular dynamics simulation using MM+ method at constant temperature ($T = 350\text{K}$). The results on the picosecond time scale are depicted on Figure 2 and their interpretation reveals the best angular rigidity for SPPD system. DPPD system indicates a damped torsional motion at 0.05 ps. On the other hand, IPPD antioxidant is very sensitive on the thermal effects for the whole investigated time range.

Another interesting conclusions may be done on the influence of the molecular structure on the maximal wavelengths (λ_{max}) corresponding to the lowest singlet-singlet (S_0-S_1) transitions. It is known that λ_{max} values measured in real systems are shifted due to environmental influences. Nevertheless, the trends calculated for a series of similar compounds in vacuum are usually preserved also in real systems. The calculated absorption spectra of studied antioxidants are depicted in Figure 3. In the examined region between 200 nm and 350 nm these records exhibit three very diffuse bands. Despite the fact that the absorption bands are a superposition of the absorption of different conformers with small energy differences ($\Delta E < kT$) and their interaction with environment, the theoretical values of λ_{max} (see Figure 2) are in good agreement with the available experimental data. In CHCl_3 , DPPD shows a shoulder at 246 nm and a peak at about 300 nm [2]. The expected lowest difference of spectral characteristics between IPPD and SPPD compounds can be explained using the dumping effect of the alkyl chain in SPPD. Otherwise, the smaller red shift of λ_{max} values is due to the perturbation of the molecular aromaticity. The presence of oxygen leads to an increase of the transition-dipole moments and to the red shift of the longest wavelength bands about 100 nm for the systems under study. The experimental results available for DPPD indicate that oxidation causes a growth of the band at 411 nm. This band shifts slowly to 415 nm and simultaneously we observe a reduction of the band at 300 nm.

Conclusion

In this article, a systematic study of antioxidants consisting of secondary amines is presented (see Figure 1). The optimal geometries, energies and electron absorption spectra of the modelled structures were obtained by semiempirical quantum-chemical methods AM1 and ZINDO/S. Influence of the chemical

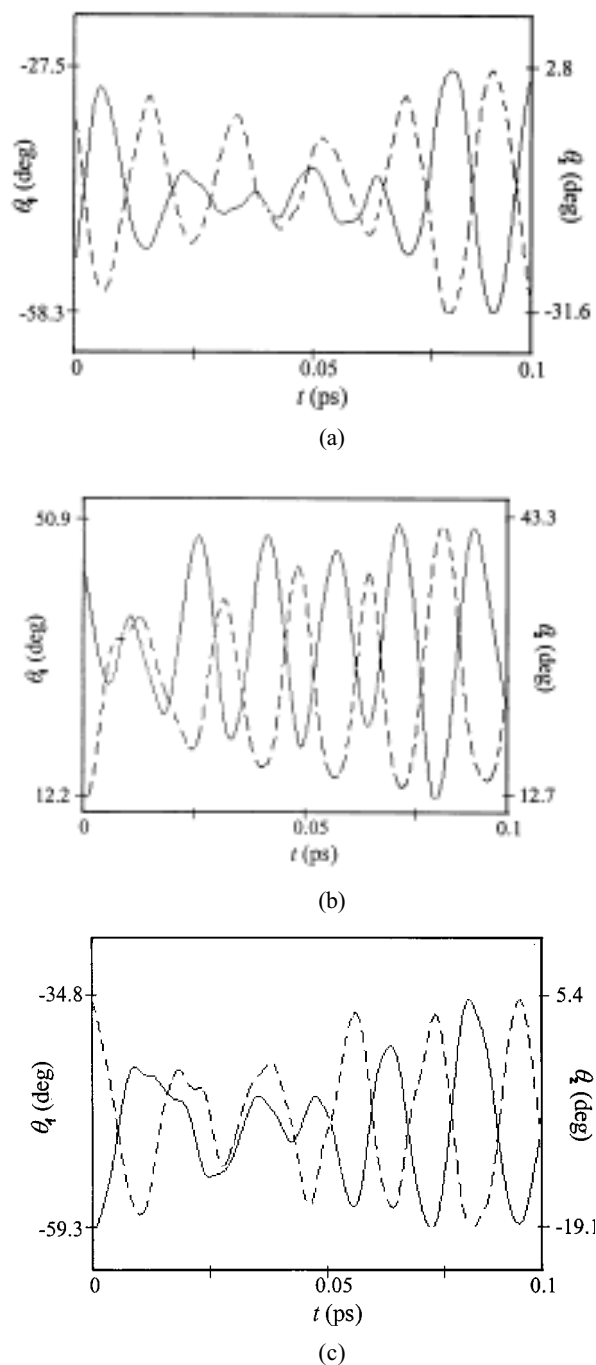


Figure 2. The molecular dynamics calculations of the time dependence of the torsional angles Θ_1 , Θ_2 at $T = 350\text{K}$ for DPPD (a), IPPD (b) and SPPD (c). The dashed line stands for the right y-axes.

modification on the energetic and electronic spectra were investigated. It seems that DPPD and SPPD compounds reveal higher energetical barriers in the antioxidant reaction scheme (see Scheme 2) than IPPD one. The molecular dynamics calculations indicate also good thermal resistance for SPPD and DPPD compounds. High thermal sensitivity is predicted for IPPD antioxidant. It is due to the presence of iso-propyl chain in the molecular skeleton and its electron-donor effect on the benzene ring. The predicted energetical and optical characteristics are in good agreement with the trends available from experiment [2, 11, 12].

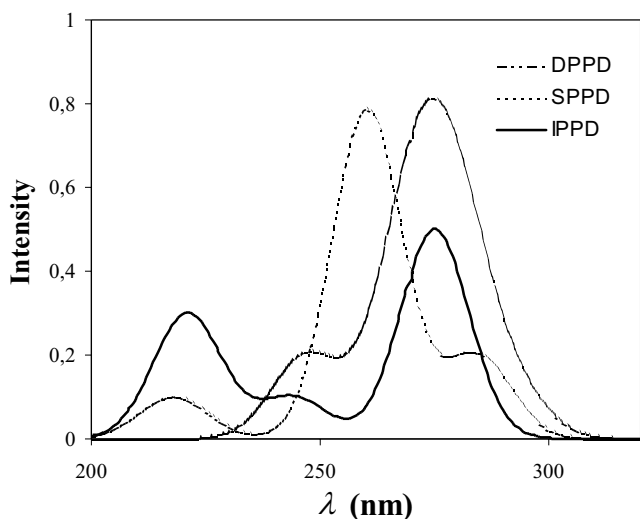


Figure 3. Simulated electronic absorption spectra of DPPD (solid line), IPPD (dotted line) and SPPD (dashed line) compounds (gaussians halfwidth of 30 nm).

It may be concluded that this type of antioxidants still represent a perspective basis for material research in polymer science and industry. However, good understanding of the reaction mechanism, energetics and molecular properties of the relevant intermediates and products is necessary for further optimal modifications of the antioxidant groups. It should lead to the improvement of their chemical and mechanical properties.

Acknowledgements

This work has been supported by Slovak Grant Agency

(Projects No. 1/0055/03 and 1/0054/03).

References

- [1] Rakovsky S., Zaikov G.: Kinetics and mechanism of ozone reactions with organic and polymeric compounds in liquid phase. New York, Nova Science **1998**.
- [2] Cataldo F.: Eur. Polym. J. **2002**, 38, 885.
- [3] Cataldo F.: Polym. Degrad. Stab. **2001**, 72, 287.
- [4] Li G.-Y., J.L. Koenig.: Polym. Degrad. Stab. **2003**, 81, 377.
- [5] Grassie N., Scott G.: Destrukcia i stabilizacia polimerov, Mir, Moskva **1988**.
- [6] www.scientific.net/0-87849-905-9/404.htm
- [7] Cataldo F.: Polym. Degrad. Stab., **1998**, 60, 223 and references therein.
- [8] Cataldo F.: Polym. Degrad. Stab., **2001**, 73, 511 and references therein.
- [9] Cataldo F., Heymann D.: Polym. Degrad. Stab., **2000**, 70, 237.
- [10] Stenberg B., Shur J., Jansson J.F.: J. Appl. Polym. Sc. Appl. Polym. Symp., **1979**, 35, 311.
- [11] Cibulková Z., Diploma work **2003**.
- [12] Cibulková Z., Šimon P.: Unpublished results - article in preparation **2003**.
- [13] Dewar M.J.S., Zoebisch E.G., Healy E.F., Stewart J.J.P.: J. Am. Chem. Soc. **1985**, 107, 3902.
- [14] Zerner M.C., Loew G.H., Kirchner R.F., Mueller-Westerhoff U.T.: J. Am. Chem. Soc., **1985**, 102 589.
- [15] Smart J.L., Marrone T.J., McCammon J.A.: J. Comp Chem. **1997**, 18 1750.
- [16] Dewar M.J.S., Yuan Y.C.: Inorg. Chem., **1992**, 29, 3881.
- [17] Dewar M.J.S., Dieter K.M.: J. Am. Chem. Soc. **1986**, 108, 8075.
- [18] Stewart J.J.P.: MOPAC 93.00 Manual, Fujitsu Limited, Tokyo, **1993**.
- [19] HYPERCHEM, rel. 3 for Windows, Hypercube, Inc. **1993**.
- [20] Borman S: Chem. Eng. News, **1990**, 68, 20.