

Torsional deformation effect on the N—H bond dissociation energy in diphenylamine

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Abstract: In this work, the influence of the inter-ring dihedral angles and their deformation on the energetics of diphenylamine molecule and its radical is investigated by the B3LYP/6-311++G** approach. Our approximated bond dissociation enthalpy of diphenylamine is 370.0 kJ mol⁻¹ and it is in good agreement with the recently published experimental data. The potential functions of both the molecule and the radical with respect to the mutual aromatic ring orientations are presented. The potential function for the molecule is of a double-barrier type, whereas the radical possesses a single-barrier function. The calculated total electronic energies are used to approximate the change of the bond dissociation enthalpy with the twisting of the dihedral angle. The dependence of the bond dissociation enthalpy on the dihedral angle is represented by a single-barrier type function. The dependence of the nitrogen atom spin density on the studied dihedral angle is also discussed.

Keywords: DFT, industrial antioxidant, BDE, diphenylamine, torsional potential energy

Introduction

Oxidation initiated by oxygen, ozone, heat and dynamic stress is the main reason of ageing and degradation of rubbers and synthetic polymers. This process is aroused by the presence of free radicals. Addition of antioxidants is one of the most used methods to decrease the rate of oxidation process (Gugumus 1990, Rabek 1990).

Antioxidants are chemical compounds inhibiting the reactive radicals formed in the oxidative reactions. The primary antioxidants comprise essentially sterically hindered phenols and secondary aromatic amines. These antioxidants act usually both through chain transfer and chain termination (Gugumus 1990, Rabek 1990, Vagánek et al. 2013). Secondary aromatic amines are widely used antioxidants in rubber industry (Cataldo 2001, 2002), being effective also as antiozonants.

In amine-type antioxidants, N—H bond dissociation enthalpy (BDE) is one of the most important parameters in the evaluation of antioxidant action (Zhu et al. 1997). In the case of secondary aromatic amines it corresponds to the reaction enthalpy of the following chemical process



It is given by Eq. 2

$$\text{BDE} = H(\text{Ar}_2\text{N}^\bullet) + H(\text{H}^\bullet) - H(\text{Ar}_2\text{N—H}) \quad (2)$$

where $H(\text{Ar}_2\text{N}^\bullet)$ stands for the total enthalpy of the formed aminyl radical, $H(\text{H}^\bullet)$ for the total enthalpy of the abstracted hydrogen atom and $H(\text{Ar}_2\text{N—H})$

is the total enthalpy of the molecule. BDE values can be determined by various experimental methods in gas or solution phase utilizing different physico-chemical principles (Ruscic et al. 1989, Ervin 2001, Seakins et al. 1992, Bordwell et al. 1993, Jonsson et al. 1994). Very satisfactory estimation of experimental BDE values can be provided by the methods of computational chemistry (Klein et al. 2006, Klein and Lukeš 2006a, 2006b, Rimarčík et al. 2011, Vagánek et al. 2013).

This work is focused on the diphenylamine (DPA) being the basis for many industrial antioxidants. DPA and its derivatives are most commonly used as stabilizers in nitrocellulose-containing explosives and propellants, in the perfumery, and as antioxidants in the rubber and elastomer industry (Drzyzga 2003). The optimized structure and atom numbering of DPA molecule are depicted in Figure 1.

If DPA or DPA derivative molecule is in the solid phase matrix, then it is plausible to assume that some dihedral angle can be changed. It is very well known that in many types of natural or synthetic compounds a change of particular torsion angle can markedly influence various molecular properties (Kortišová et al. 2005). Therefore, the main goal of this work is to investigate the influence of torsional deformation on the energetics of DPA molecule by means of computational chemistry.

Computational details

All calculations were performed using Gaussian 03 program package (Frisch et al. 2003). The geom-

etry of each compound and radical structure was optimized in the gas phase using density functional theory (DFT) method with B3LYP (Becke's three parameter Lee-Yang-Parr) (Lee et al. 1988) functional without any constraints (energy cut-off of 10^{-5} kJ mol $^{-1}$, final RMS energy gradient under 0.01 kJ mol $^{-1}$ Å $^{-1}$). B3LYP functional represent widely applied approach for the theoretical study of the reaction enthalpies. For mono-substituted phenols, thiophenols and anilines, it has been found that B3LYP functional provided BDEs in very good accordance with available experimental and/or theoretical results (Klein et al. 2006, Klein and Lukeš 2006a, 2006b, Rimarčík et al. 2011, Vagánek et al. 2013). Calculations were performed in the 6-311++G** (Binkley et al. 1980) basis set. The optimized structures of DPA molecule and radical, without fixing any internal coordinates, were confirmed to be real minima by vibrational analysis (no imaginary frequency). Total enthalpies of these structures were calculated for 298.15 K. Total enthalpy, $H(H^\bullet)$, and total electronic energy, $E(H^\bullet)$, values of the hydrogen atom obtained by above mentioned approach are of -1314.96 kJ mol $^{-1}$ and -1318.68 kJ mol $^{-1}$, respectively.

Results and discussion

Individual structures, characterized by dihedral angle ϕ (C7-C2-N1-C2'), were built by fixing the dihedral angle θ (C2-N1-C2'-C3') and by variation of ϕ angle with the step of 10 degrees, see Figure 1. We have chosen the 0–180 degrees interval of ϕ angle variation. The θ dihedral angle was fixed at its optimized value (26 degrees).

Dependence of the DPA total electronic energy and nitrogen atom spin density on ϕ dihedral angle

In this paper, the dependence of the total electronic energy on the dihedral angle ϕ in both the molecule

and the radical of DPA has been evaluated. For the sake of simplicity, the difference against the total electronic energy for the optimal geometry is depicted instead of absolute values. As shown in Figure 2, the dependence for the molecule can be characterized by a double-barrier potential function. The bottom of the deeper potential well represents the optimal geometry of DPA with values of the both studied dihedral angles being 26° while molecule possesses the C2 symmetry. Changing one of these dihedral angles is associated with a steep ascent of the total electronic energy over one potential barrier on each side of the potential well. Both potential barriers are ca 10 kJ mol $^{-1}$ high and they are localized at the torsional angle values of 70–80° and 150–160°. The energy difference of 10 kJ mol $^{-1}$ is equivalent to the temperature of 1202 K, which is highly above the decomposition temperature of DPA, thus under standard conditions the studied torsion angle in DPA remains around the value for the optimal geometry. The shallow potential well at 120° with a depth of ca 4 kJ mol $^{-1}$ represents a geometry stabilized by the energy of partial delocalization while the destabilizing repulsion forces between ortho-hydrogens and the hydrogen of the amine group are acceptable. The amine hydrogen atom represents one of obstacles limiting the free rotation thus one should expect a different shape of potential function after its abstraction. In the Figure 2 it is well shown that the optimal geometry of both the molecule and the radical bears the same ϕ value. However, the radical formation and change in the electronic structure greatly affects the potential well making it narrower and almost 28 kJ mol $^{-1}$ deep. The potential function is characterized by a wide single potential barrier. Due to its height, one should assume that the only feasible values of the torsion angle in DPA radical are in the interval from 0° to 50°.

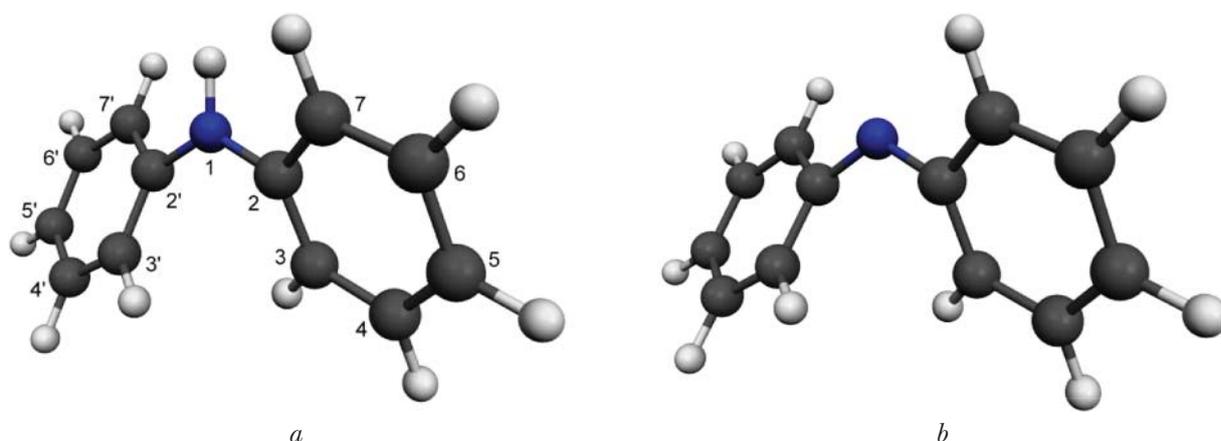


Fig. 1. The B3LYP/6-311++G** optimized structure and atom numbering of diphenylamine molecule (a) and its radical (b). Both are of C2 symmetry. Visualised in Molekel 4.3 (Flükiger et al. 2002)

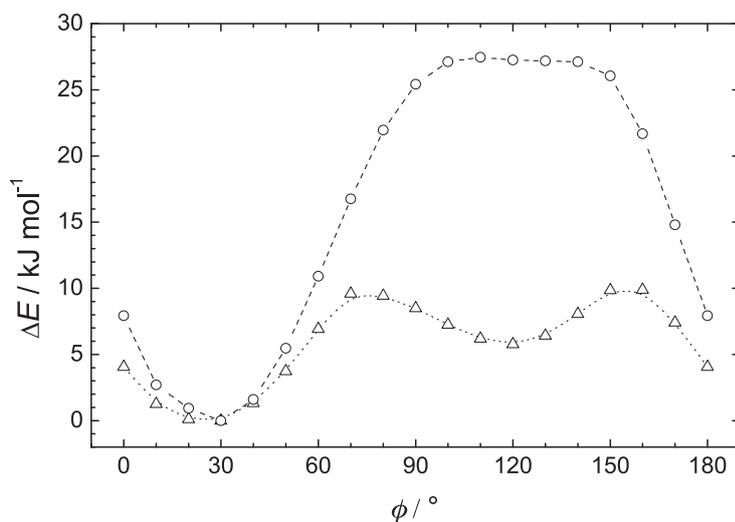


Fig. 2. The dependence of the calculated ΔE values on dihedral angle ϕ in the DPA molecule (triangles, dotted line) and in the radical (circles, dashed line).

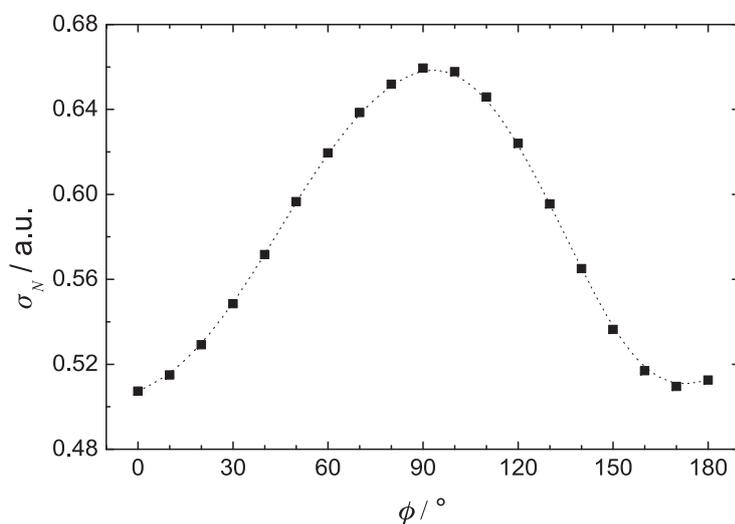


Fig. 3. The dependence of the calculated spin density on the nitrogen atom on the dihedral angle ϕ in DPA radical.

The spin density is a useful quantity characterizing the radical properties. Therefore the spin density on the nitrogen atom of DPA radical was evaluated and its dependence on the dihedral angle is depicted in the Figure 3. Despite the stabilisation force of the unpaired electron delocalisation in the radical, the optimal structure is not the one with the highest delocalisation. The repulsion energy between the close placed *ortho*-hydrogens in co-planar structure acts against the stabilising delocalisation energy. The resulting value of the torsion angle of 28.6° represents the equilibrium between these two forces. The torsion angle of ca 90° allows only minor delocalisation and is characterized by the highest spin density on the nitrogen atom.

Agreement between calculated bond dissociation enthalpies approximated from the total electronic energies and experimental values

In this article, the bond dissociation enthalpies approximated by using the total electronic energies, $BDE(E)$, were calculated. They have been obtained by Eq. 2 by replacing the total enthalpies with the total electronic energies E . The N—H $BDE(E)$ value, corresponding to the optimal geometries of the DPA molecule and radical, reaches $370.0 \text{ kJ mol}^{-1}$. If the Eq. 2 is used, then the N—H BDE acquires the value of $340.6 \text{ kJ mol}^{-1}$. Thus the difference between N—H $BDE(E)$ and N—H BDE values is 29.4 kJ mol^{-1} . A very similar shift between $BDE(E)$ and BDE values has been found for mono-substituted phenols (Klein and Lukeš 2006a) and anilines (Vagánek et al. 2013),

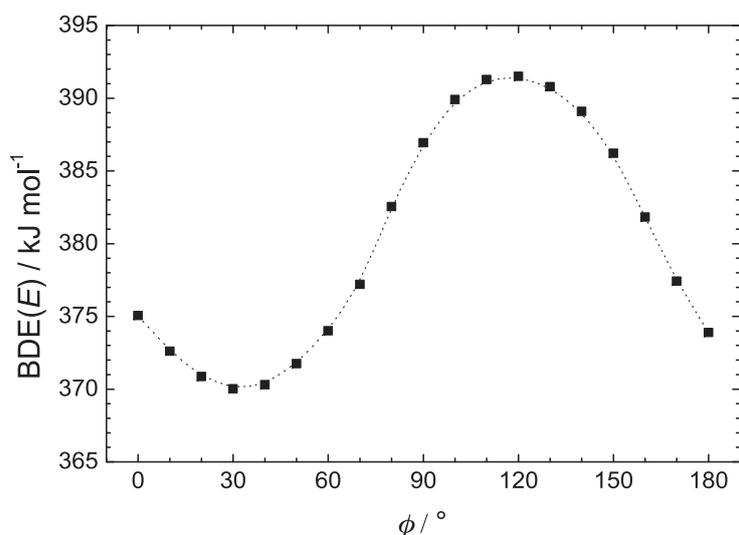


Fig. 4. The dependence of the calculated N—H BDE(E) values on dihedral angle ϕ .

29 and 30 kJ mol⁻¹, respectively. In the literature, there are also available some experimental and theoretical N—H BDE values for DPA. Bordwell et al. (1993) estimated the DPA N—H BDE value of 366.1 kJ mol⁻¹. They applied the equilibrium acidities (p*K*_a) and oxidation potential (E_{ox}) values of the conjugated anions measured in DMSO for BDE calculation. Zhu et al., employing the same method, obtained the value of 366 kJ mol⁻¹ (Zhu et al. 1996). Standard deviations of these BDEs are usually in 4–8 kJ mol⁻¹ range (Zhu et al. 1996, Bordwell et al. 1993). MacFaul et al. found the value of 373 kJ mol⁻¹ by means of the photoacoustic calorimetry method (MacFaul et al. 1997). Measurements were carried out in benzene with the standard deviation of 4 kJ mol⁻¹. Gomes et al. (2004) calculated the gas-phase value of 355 kJ mol⁻¹ at (RO)B3LYP/6-311+G(2d,2p)//(U)B3LYP/6-31G* level of theory. Considering the standard deviations of the above mentioned experimental values, our BDE(E) is in good agreement with experimental solution phase BDEs. This trend was also observed in the case of phenols (Klein and Lukeš 2006b) and thiophenols (Rimarčík et al. 2011).

Dependence of BDE(E) on dihedral angle ϕ

Calculated BDE(E) values corresponding to the structures given by a ϕ angle are shown in the Figure 4. In the Figure 4, it can be seen that the difference between the highest and the lowest BDE(E) values reached 21.5 kJ mol⁻¹. Thus the influence of the torsional deformation on the BDE(E) is considerable in DPA molecule. The lowest BDE(E) value corresponds to the dihedral angle ϕ of 30 degrees and the highest value to $\phi = 120^\circ$. Accordingly, the dependence of BDE(E) on ϕ , ranging from 0 to 180 degrees shows two extremes. Figure 4 clearly shows a

90 degrees interval between the minimum and the maximum. In the range of 20–40 degrees the BDE(E) alternation is no more than 1 kJ mol⁻¹. The similar trend is also observable in the case of the maximum. In the interval from 110° to 130°, the value of BDE(E) varies within ca 1 kJ mol⁻¹.

Conclusion

Presented results are in accordance with the published experimental data, thus B3LYP/6-311++G** approach can be considered as applicable for the study of energetics of the diphenylamine. Due to the repulsion energy between the hydrogen atoms of the rings, the optimal structure of diphenylamine is not co-planar, however the plane of the ring is twisted with respect to the plane of the C—N—C linkage. The found potential functions describe the relationship between this angle and the total electronic energy of both diphenylamine species. We have shown that the potential function of diphenylamine is of a double-barrier type, whereas the one of the radical is of a single-barrier type. The dependence of the bond dissociation enthalpies on the dihedral angle is represented by the single-barrier type function. The dependence of the nitrogen atom spin density on the studied dihedral angle consists of one minimum and one maximum corresponding to the co-planar and perpendicular conformation, respectively. Consequently, the optimal geometry is not characterized by the lowest spin density on the hydrogen atom. The results obtained in this work show that changes in geometry caused e.g. by placing the molecule into the solid phase matrix are not negligible and they also affect the value of bond dissociation enthalpy. This fact opens possibilities for further and more detailed studies.

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