ORIGINAL PAPER

Mechanistic study of electrochemical oxidation of 2,5-diethoxy-4morpholinoaniline in aqueous solutions: hydrolysis, trimerization, and hydroxylation processes

Hadi Beiginejad · Davood Nematollahi

Received: 7 May 2014/Accepted: 2 January 2015 © Springer-Verlag Wien 2015

Abstract The electrochemical oxidation of 2,5-diethoxy-4-morpholinoaniline has been studied in various pHs using cyclic voltammetry and controlled potential coulometry. The results indicate that the electrochemically generated *p*quinonediimine participates in different types of reactions (hydrolysis, hydroxylation, and trimerization). Instability of the produced *p*-quinonediimine depends on its structure, higher nucleophilicity of 2,5-diethoxy-4-morpholinoaniline, and pH of solution. In lower pH range, rate of hydrolysis is faster than hydroxylation and dimerization. In intermediate pHs rate of the dimerization is faster than hydrolysis and hydroxylation, and in the strongly alkaline solution, rate of the hydroxylation is faster than hydrolysis and dimerization. The effect of the charge of reaction site (C_1) and $N_1=C_1$ bond order (Wiberg bond indices) on the hydrolysis rate were studied. Calculations were performed using density functional theory B3LYP level of theory and 6-311+G(p,d) basis set.

H. Beiginejad (🖂)

Faculty of Science, Department of Chemistry, Malayer University, 65174 Malayer, Iran e-mail: beiginejad.hadi@yahoo.com; h.beiginejad@malayeru.ac.ir

D. Nematollahi

Faculty of Chemistry, Bu-Ali-Sina University, 65174 Hamedan, Iran

Graphical abstract





Introduction

Electrochemistry provides very versatile means for the electrosynthesis and mechanistic studies [1-6]. Using electrochemical methods with a wide time window (submicroseconds to hours) thermodynamic and kinetic information about the reactions of organic and inorganic species were obtained [7-12]. It is known that cyclic voltammetry is a powerful technique for investigation of electrochemical reactions that are coupled with chemical reactions [13, 14]. Electrochemical studies of amines were performed at various conditions such as aqueous and nonaqueous solvent or at various pHs [15-21]. Electrochemical oxidation mechanism of aromatic amines is quite complex, and leads to a variety of products depending on their structure and electrolysis conditions [22, 23]. Investigations indicated that dimerization, trimerization, hydrolysis, and hydroxylation can occur in electrochemical oxidation of amines which is highly dependent on pH of solution [24, 25]. Along with our previous works in electrochemical study of amines [23–28], diversity of behavior in the electrochemical oxidation of 2,5-diethoxy-4-morpholinoaniline (2,5-DEMA, 1) at various conditions and also the importance of Schiff base reaction [29] prompted us to studying electrochemical oxidation of 2,5-DEMA at various conditions using cyclic voltammetry (CV) and controlled-potential coulometry. The results show that in all pHs electrochemically generated p-quinonediimine $(10x^+ \text{ or } 10xH^{2+})$ is unstable and participates in different types of reactions based on solution's pH. Produced *p*-quinonediimine hydrolyzed in lower pH range, trimerized in intermediate pHs, and hydroxylated in strong alkaline solution. To investigate the hydrolysis reaction rate of electrochemically generated p-quinonediimines $(10x^+ \text{ or } 1Hox^{2+})$, the effect of positive charge of reaction site (C_1) and bond order of $C_1=N_1$ bonds were studied and discussed. Calculations were performed using B3LYP level of theory and 6-311+G(p,d) basis set. Also the Wiberg bond indices (WBI) of C₁=N₁ bond and charge of reaction site were analyzed with the natural bond orbital (NBO) method at mentioned level of theory.

Results and discussion

Electrochemical behavior in pH 1–9

The cyclic voltammogram (CV) recorded for 1.0 mM of 2,5-diethoxy-4-morpholinoaniline (2,5-DEMA) in water/ acetonitrile (50/50) solution containing 0.2 M acetate buffer (pH 4.3) is shown in Fig. 1. The CV exhibits one anodic peak (A_1) at 0.30 V and a cathodic peak (C_1) at 0.20 V vs. Ag/AgCl, respectively which corresponds to the transformation of 2,5-DEMA (**1H**⁺) to *p*-quinonediimine (**1ox**⁺) and vice versa within a quasi-reversible two-electron process [26]. Under this condition, the peak current



Fig. 1 CV 1.0 mM of 2,5-DEMA in water/acetonitrile (50/50) solution containing 0.2 M acetate buffer (pH 4.3); scan rate: 50 mV s⁻¹, $t = 25 \pm 1$ °C

ratio (I_{pC1}/I_{pA1}) is about one that can be considered as a criterion for the stability of *p*-quinonediimine $10x^+$ produced at the surface of electrode.

More data were obtained by changing the concentration and scan rate. Obtained CVs show that the peak current ratio (I_{pC1}/I_{pA1}) decreases and C_0 peak appears at less positive potentials upon increasing the concentration of 2.5-DEMA (1 H^+) or decreasing potential scan rate. Figure 2 exhibits the effect of concentration of $1H^+$ on the normalized CVs of $1H^+$ in water/acetonitrile (50/50) solution containing 0.2 M acetate buffer (pH 4.3). Normalized CVs are obtained by dividing the current by the concentration (I/c). As it is shown in Fig. 2, the peak current ratio (I_{pCl}/I_{pAl}) is dependent on the concentration of 2,5-DEMA $(1H^+)$. Increasing substrate concentration causes the peak current ratio (I_{pC1}/I_{pA1}) to decrease proportionally. Using previous works on the electrochemical oxidation of 2,5-DEMA [26, 27] and the present data, it can be said that the cathodic peak C_0 is related to the electrochemical reduction of the product which is produced after trimerization reaction.

Recorded CV for 1.0 mM of 2,5-DEMA ($\mathbf{1H}^+$) in water/ acetonitrile (50/50) solution containing 0.1 M perchloric acid (pH 1.0) is shown in Fig. 3. The voltammogram indicates one anodic peak A_1 at 0.44 V and two cathodic peaks C_1 and C_2 at 0.39 and 0.26 V vs. Ag/AgCl, respectively. C_1 and A_1 are counterpart and correspond to the transformation of $\mathbf{1H}_2^{2+}$ to *p*-quinonediimine ($\mathbf{1Hox}^{2+}$) and vice versa within a two-electron, two-proton process. The current of the cathodic peak C_1 depends on the potential scan rate and increases with increasing it. This result



Fig. 2 Normalized CVs of 2,5-DEMA in water/acetonitrile (50/50) solution containing 0.2 M acetate buffer (pH 4.3) at various concentrations. *a* 1.0 mM, *b* 2.0 mM, and *c* 5.0 mM. Scan rate = 50 mV s⁻¹, $t = 25 \pm 1$ °C. *Inset* cyclic voltammograms of *a* the first and *b* the second cycle of 1.0 mM 2,5-DEMA (**1H**⁺) in water/acetonitrile (50/50) solution containing 0.2 M acetate buffer (pH 4.3), scan rate 25 mV s⁻¹, $t = 25 \pm 1$ °C



Fig. 3 CVs 1.0 mM of 2,5-DEMA in water/acetonitrile (50/50) solution containing 0.1 M perchloric acid (pH 1.0); scan rate: 50 mV s⁻¹, $t = 25 \pm 1$ °C

indicates that 1Hox^{2+} in the timescale of our experiments is unstable and participates in following chemical reactions. Previous works show that in this condition the hydrolysis is a chemical following reaction and the cathodic peak C_2 relates to the electrochemical reduction of the product which is produced after hydrolysis reaction [26, 27].

Comparing Figs. 1 and 3 shows that instability of the produced *p*-quinonediimine increases upon decreasing pH. It was reported that based on structures of species, rate of hydrolysis for some amines increases with increasing pH. while it decreased for some others [28]. To explain the observed difference in the electrochemical oxidation behavior in lower pH range and intermediate pHs, computational study was used. In more acidic pHs (pH 1–3), there is a direct relation between acidity and instability of *p*-quinonediimine $(10xH^{2+})$. Our reported results show that the N=C bond order (WBI) and charge on the reaction site (C_1) have significant roles in the hydrolysis reaction rate [28]. Increasing the positive charge on C_1 atom and consequently increasing its electrophilicity makes it more susceptible to nucleophilic attack by hydroxide ion or water which causes increasing hydrolysis reaction rate. Also $=NR_2$ is a leaving group and the hydrolysis rate is inversely proportional to the strength of N=C bonds, in which the lower the WBI of N=C bond, the higher the rate of the hydrolysis reaction [28]. The positive charge on the reaction sites (C₁) and WBIs of C₁=N₁ bonds for $10x^+$ and 10xH²⁺ were calculated using density functional theory (DFT) and natural bond orbital (NBO) analysis (Fig. 4). As can be seen not only charge on C_1 in $10xH^{2+}$ is more positive than charge on C_1 in **1ox**⁺ but also WBI of $C_1=N_1$ bond in $10xH^{2+}$ is lower than that of $10x^+$. According to these results, it could be concluded that although higher



Fig. 4 Calculated charge on the reaction sites (C_1) and WBIs $N_1=C_1$ bonds, using B3LYP level of theory and 6 - 311G + (p,d) basis set



Fig. 5 CV 1.0 mM of 2,5-DEMA in water/acetonitrile (50/50) solution containing 0.2 M phosphate buffer (pH 7.0); scan rate: 50 mV s⁻¹, $t = 25 \pm 1$ °C. *Inset*: variation of peak current ratio (I_{C1}/I_{A1}) vs. scan rate

nucleophilicity of 2,5-DEMA $(1H_2^{2+})$ decreases in more acidic solution due to protonation of 1 which causes decreasing rate of dimerization, protonation of $10x^+$ and formation of $10xH^{2+}$ in this condition cause increasing instability of produced *p*-quinonediimine [26, 28]. In other words, using this data it could be concluded that in the intermediate pHs rate of the dimerization is faster than hydrolysis, and in the lower pH range the rate of the hydrolysis is faster than dimerization.

CV of 2,5-DEMA (1) in water/acetonitrile (50/50) solution containing 0.2 M buffer $H_2PO_4^{-}/HPO_4^{2-}$ (pH 7.0) is shown in Fig. 5. As shown in this figure the CV exhibits one anodic peak A_1 at 0.19 V and two cathodic peaks C_1 and C_0 at 0.155 and -0.02 V vs. Ag/AgCl, respectively. The anodic and cathodic peaks A_1 and C_1 are counterpart

and correspond to the transformation of 1 to the *p*-quinonediimine $10x^+$ and vice versa within a quasi-reversible two-electron, one-proton process [26]. As can be seen the peak current ratio (I_{pC1}/I_{pA1}) is less than one and increases upon increasing the scan rate (inset of Fig. 5). This result indicates that $10x^+$ in the timescale of our experiments is unstable and participates in following chemical reactions. The new cathodic peak C_0 is related to the electrochemical reduction of the product which is produced after trimerization [26]. Comparing CVs 1.0 mM of 2,5-DEMA in pH 4.3 and 7 shows although there are same following chemical reaction after electrochemical oxidation of 2.5-DEMA, but the peak current ratio (I_{pC1}/I_{pA1}) in pH 4.3 is more than that of pH 7.0 which is shown that rate of the following chemical reaction in pH 4.3 is lower than that of pH 7.0. Electrochemical oxidation of 2,5-DEMA (1) at various pHs shows that the electrode surface reaction at pH > 5.23, corresponds to the two-electron, one-proton process (Scheme 1) [26]. Electrochemical oxidation of various species in the presence different nucleophiles indicates that the peak current ratio (I_{pC}/I_{pA}) decreases upon increasing power nucleophilicity of nucleophiles [31, 32]. In other words, in pH upper than 5.23, $1H^+$ loses its proton and converts to its neutral form (1) therefore, power nucleophilicity of it increases which causes increasing rate of dimerization as following chemical reaction and the peak current ratio (I_{pC1}/I_{pA1}) decreases.

Electrochemical behavior in strong alkaline pHs (*pH 10–13*)

Figure 6 shows cyclic voltammogram 1.0 mM of 2,5-DEMA (1) in aqueous solution containing 0.01 M sodium hydroxide (pH 12). As it is shown in this figure, at the scan rate of 100 mV/s, the CV exhibits the feature of an irreversible electron-transfer process with an anodic peak (A_1) at -0.015 V vs. Ag/AgCl, which corresponds to the transformation of 1 to its *p*-quinonediimine $(10x^+)$ [26]. The cyclic voltammogram behavior strongly depends on the scan rate, and the C_1 peak (counterpart of the A_1) appears and its current increases with increasing the scan rates. In addition, height of the cathodic peak C_0 decreases by increasing the potential scan rate. This CV shows that $10x^+$ is unstable and participates to following chemical reaction. The second cycle of the cyclic voltammogram for this solution (Fig. 6, curve b) shows a new anodic peak (A_0) at -0.33 V. The cathodic peak C_0 and its corresponding anodic peak (A_0) in the second cycle of the cyclic voltammogram correspond to the reduction and oxidation of the product that is produced at the surface of the GC electrode.

It is probably in the following chemical reaction $10x^+$ hydrolyzed and converts to *p*-benzoquinone 1a (Scheme 1). To synthesize 1a, using method which is

reported in the published paper [26], 80 cm³ buffer $H_3PO_4/H_2PO_4^-$ (0.2 M, pH 2.0) containing 0.05 mmol of **1** was subjected to electrolysis at 0.40 V vs. Ag/AgCl in a divided cell. The electrolysis was terminated when the current decayed to 5 % of its original value and **1a** was extracted by ethylacetate. Figure 7, curve b shows obtained cyclic voltammogram 0.5 mM of **1a** in aqueous solution containing 0.01 M sodium hydroxide. By comparing CVs of **1a** and **1** under the same condition the idea of hydrolysis reaction as a chemical following reaction is rejected.

Based on what was reported in the literature, dimerization as a following chemical reaction can be recognized by the use of changing the concentration of studied species, in which dilution solution of 2,5-DEMA (1) and consequently decreasing the rate of dimerization causes increasing the peak current ratio (I_{pC1}/I_{pA1}) [26]. To study effect of concentration, normalized cyclic voltammograms of 1 at various concentrations in pH 12 were obtained. Normalized CVs are obtained by dividing the current by the concentration (I/c). Figure 8 shows that the peak current ratio (I_{pC1}/I_{pA1}) is independent of concentration of 2,5-DEMA (1). These data reject the dimerization reaction after the electron transfer process as the first following chemical reaction.

Controlled-potential coulometry 80 cm³ containing 0.30 mmol of **1** in aqueous solution (0.1 M sodium hydroxide, pH 13) at -0.05 V vs. Ag/AgCl was performed (Fig. 9). All three anodic and cathodic peaks (A_1 , A_0 , and C_0) disappear when the charge consumption becomes about $2e^-$ per molecule of **1** and the final product was analyzed using mass spectroscopy (MS).

Our experiences on electrochemical oxidation of amines at various conditions [24–28], diagnostic criteria of cyclic voltammetry and controlled-potential coulometry (Figs. 6, 7, 8, 9), consumption of two electrons per molecule of 1and the mass spectrum of isolated product (m/z = 551)allow us to propose ECEC pathway for the electrochemical oxidation of 2,5-DEMA (1) in strongly alkaline pHs (Scheme 2). As is shown in Scheme 2, the electrochemical oxidation of 2.5-DEMA (1) leads to the formation of pquinonediimine $(10x^+)$. Via a Michael addition reaction with hydroxide ion and aromatization, $10x^+$ is converted to 2a. The oxidation of compound 2a is easier than the oxidation of 1 by virtue of the presence of an electrondonating group [30]. In the next step, the generated pquinonediimine $20x^+$ is subjected to another Michael addition reaction with 1 and converts to the final product **2b**. It should be noted that, in the mass spectra of **2b**, the molecular ions [M + 4H] was recorded (Fig. 10). This mass is related to protonation of the quinonic moiety and amino groups. Obtained results show that in the power alkaline solution (pH 10-13) rate of the hydroxylation is faster than hydrolysis and dimerization.







Conclusion

In the present work, electrochemical oxidation of 2,5-diethoxy-4-morpholinoaniline (2,5-DEMA) has been studied in various pHs using cyclic voltammetry and controlledpotential coulometry. The results show that 2,5-DEMA (1) is oxidized in aqueous solutions to its *p*-quinonediimine ($10x^+$ or $10xH^{2+}$). Obtained the peak current ratio (I_{pC1}/I_{pA1}) show that the produced *p*-quinonediimine is unstable in all pHs and participate in hydrolysis, trimerization, and



Fig. 6 CVs of *a* the first and *b* the second cycle of 1.0 mM 2,5-DEMA (1) in aqueous solution containing 0.01 M sodium hydroxide (pH 12); scan rate: 100 mV s⁻¹, $t = 25 \pm 1$ °C



Fig. 7 *a* CV 1.0 mM of 2,5-DEMA and *b* cyclic voltammogram 1.0 mM of **1a** in aqueous solution containing 0.01 M sodium hydroxide (pH 12); scan rate: 100 mV s⁻¹, $t = 25 \pm 1$ °C

hydroxylation reactions depend on solution's pH. The reaction mechanisms for the electrochemical oxidation of 2,5-DEMA (1) in different pHs are presented in Schemes 1 and 2. Instability of the produced *p*-quinonediimine depends on the its structure, higher nucleophilicity of 2,5-DEMA (1) and pH of solution. The electrochemical oxidation of 2,5-DEMA (1) at various pHs shows that rate of following chemical reaction indicates final product. In the power acidic solution rate of hydrolysis is faster than hydroxylation and dimerization. In the intermediate pHs rate of the dimerization is faster than hydrolysis and hydroxylation, and in the power alkaline solution rate of the hydroxylation is faster than hydrolysis and dimerization. The effect of charge of reaction site (C_1) and $N_1=C_1$ bond orders (Wiberg bond indices, WBI) on the stability of produced p-quinonediimine were studied. Calculations



Fig. 8 Normalized cyclic voltammograms of 2,5-DEMA in aqueous solution containing 0.01 M sodium hydroxide (pH 12) at various concentrations. Scan rate = 250 mV s^{-1} , $t = 25 \pm 1 \text{ °C}$



Fig. 9 Cyclic voltammograms of 2,5-DEMA (0.30 mmol) during controlled potential coulometry at -0.05 V vs. Ag/AgCl in aqueous solution containing 0.1 M NaOH, after the consumption of: *a* 0 C, *b* 11 C, *c* 22 C, *d* 33 C, *e* 44 C, and *f* 55 C. Scan rate: 50 mV s⁻¹, $t = 25 \pm 1$ °C. *Inset*: variation of peak current (I_{A1}) vs. consumed charge

were performed using density functional theory (DFT) B3LYP level of theory and 6-311+G(p,d) basis set.

Materials and methods

Cyclic voltammetry and controlled-potential coulometry were performed using micro Autolab potentiostat/galvanostat. The working electrode used in the voltammetry experiments was a glassy carbon disk (1.8 mm diameter) and a platinum wire was used as the counter electrode. The

Scheme 2

Strong alkaline pHs (pH = 10 - 13)



working electrode used in controlled-potential coulometry was an assembly of four ordinary carbon rods (31 cm² from KIGCO, Mashhad, Iran), placed as single rods in the edges of a square with a distance of 3 cm. The carbon rods are washed with acetone and distilled water before starting electrolysis. A large platinum gauze was used as counter electrode. The experiment was carried out at a temperature of 25 ± 1 °C. The working electrode potentials were measured vs. standard Ag/AgCl (all electrodes from AZAR Electrode). Also all chemicals were reagent grade materials, from Aldrich and E. Merck and were used without further purification.

Computational study

Using Gaussian 03 [33] the geometries of all species investigated here, in the gas-phase were fully optimized at the DFT (B3LYP) level of theory [34, 35]. The standard $6-311+G^{**}$ basis set was used for geometry optimization and vibrational frequency analyses. A starting molecular- mechanics structure for the ab initio calculations was obtained using the HyperChem 5.02 program (MM⁺ method). [36]. Also natural bond orbital (NBO) analyses [37] were carried out at the mentioned levels of theory.

Electroorganic synthesis of 2,5-diethoxy-p-benzoquinone (*Ia*) A phosphate buffer solution (80 cm³, 0.2 M, pH 2.0) containing 0.05 mmol of 2,5-diethoxy-4-morpholinoaniline (1) was subjected to electrolysis at 0.40 V vs. Ag/AgCl in a divided cell. The electrolysis was terminated when the current decayed to 5 % of its original value. The product was extracted by ethyl acetate and was washed with water. After drying, the product was characterized by IR, and structure of **1a** was confirmed by comparing the results with the literature report [26].

Electroorganic synthesis of 2-amino-4-(2,5-diethoxy-4-

morpholinophenylamino)-3,6-diethoxy-5-morpholinophenol (**2b**, $C_{28}H_{42}N_4O_7$) Alkaline solution (80 cm³) containing 0.1 M NaOH (pH 13.0) and 0.05 mmol of 2,5-diethoxy 4-morpholinoaniline (**1**) was subjected to electrolysis at -0.05 V vs. Ag/AgCl in a divided cell. The electrolysis was terminated when the current decayed to 5 % of its original value. After evaporation of water, final product was extracted with ethanol and analyzed using mass spectroscopy (MS).

References

- 1. Costentin C (2008) Chem Rev 108:2145
- 2. Houmam A (2008) Chem Rev 108:2180
- 3. Sun JJ, Wu Y, Song JF (2014) Electrochim Acta 115:386
- 4. Duan X, Tian L, Liu W, Chang L (2013) Electrochim Acta 94:192
- 5. Rafiee M, Nematollahi D (2007) Electroanalysis 19:1382
- Saraswat A, Sharma LK, Singh S, Singh RKP (2013) Synth Met 167:31
- 7. Nematollahi D, Forooghi Z (2003) Electroanalysis 15:1639
- Bard AJ, Faulker LR (2001) Electrochemical Methods, 2nd edn. Wiley, New York
- 9. Rafiee M, Nematollahi D (2008) Electrochim Acta 53:2751
- Fotouhi L, Tammari E, Asadi S, Heravi MM, Nematollahi D (2009) Int J Chem Kinet 41:426
- 11. Esmaili R, Nematollahi D (2012) J Electrochem Soc 159:H792
- Nematollahi D, Bamzadeh M, Shayani-Jam H (2010) Chem Pharm Bull 58:23
- Greef R, Peat R, Peter LM, Pletcher D, Robinson J (1990) Instrumental methods in electrochemistry. Ellis Horwood Limited, New York
- Saveant JM (2006) Elements of molecular and biomolecular electrochemistry. John Wiley & Sons, Jersey
- Esmaili R, Varmaghani, Nematollahi D (2012) J Electrochem Soc 159:H680

- 16. Nematollahi D, Maleki A (2009) Electrochem Commun 11:488
- 17. Wang G, Fu X, Huang J, Wu L, Deng J (2011) J Electroanal Chem 661:351
- Kadar M, Nagy Z, Karancsi T, Farsang G (2001) Electrochim Acta 46:3405
- Miras MC, Silber JJ, Serno L (1986) J Electroanal Chem 2019:367
- 20. Dvorak V, Nemec I, Zyka J (1967) Microchem J 12:324
- Salavagione HJ, Arias J, Garces P, Morallon E, Barbero C, Vazquez JL (2004) J Electroanal Chem 565:375
- 22. Steckan E, Baizer MM, Lund H (eds) (1991) Organic electrochemistry, an introduction and a guide. Marcel Dekker, New York, p 15
- 23. Esmaili R, Nematollahi D (2011) Electrochim Acta 56:3899
- 24. Beiginejad H, Nematollahi D, Varmaghani F (2013) J Electrochem Soc 160:H41
- Nematollahi D, Shayani-Jam H, Alimoradi M, Niroomand S (2009) Electrochim Acta 54:7407
- 26. Beiginejad H, Nematollahi D (2013) Electrochim Acta 114:242
- 27. Beiginejad H, Nematollahi D (2014) J Org Chem 79:6326
- Beiginejad H, Nematollahi D, Varmaghani F, Bayat M (2013) J Electrochem Soc 160:H469
- 29. Kirdant AS, Magar BK, Chondhekar TK (2012) J Chem Biol Phys Sci 2:147
- Beginejad H, Nematollahi D, Varmaghani F, Shayani-Jam H (2013) Monatsh Chem 144:1481
- Beiginejad H, Nematollahi D, Varmaghani F, Bayat M (2013) J Electrochem Soc 160:G3001
- 32. Varmaghani F, Nematollahi D, Mallakpour S, Esmaili R (2012) Green Chem 14:963
- 33. Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox JE, Burant JC, Millam JM, Iyengar SS, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson GA, Nakatsuji H, Hada M. Ehara M. Tovota K. Fukuda R. Hasegawa J. Ishida M. Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox JE, Hratchian HP, Cross JB, Bakken V, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski J, Ayala PY, Morokuma K, Voth GA, Salvador P, Dannenberg JJ, Zakrzewski VG, Dapprich S, Daniels AD, Strain MC, Farkas O, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Ortiz JV, Cui Q, Baboul AG, Clifford S, Cioslowski J, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson BG, Chen W, Wong MW, Gonzalez C, Pople JA (2003) Gaussian 03, revision B. 04. Gaussian, Inc., Pittsburgh
- 34. Becke AD (1993) J Chem Phys 98:5648
- 35. Lee C, Yang W, Parr RG (1988) Phys Rev B 37:785
- 36. HyperChem (1997) Release 5.02. Hypercube Inc., Gainesville
- Glendening ED, Badenhoop JK, Reed AE, Carpenter JE, Bohmann JA, Morales CM, Weinhold F (2001) NBO 5.0. Theoretical Chemistry Institute, University of Wisconsin, Madison