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CYCLIC VOLTAMMETRY AND DFT STUDIES OF SOME TRIPHENYLHYDRAZINE

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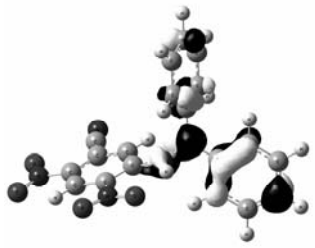
The redox behaviour of two derivatives from hydrazine, compounds 2,2-diphenyl-1-(2,4-dinitro-5-cianophenyl)hydrazine (A) and 2-(4-nitrophenyl)-2-phenyl-1-(2,4-dinitrophenyl)hydrazine (B), has been investigated in this work by using cyclic voltammetry and diferential pulse voltammetry techniques. Two different media were used, with no methoxide ion and with methoxide ion in order to investigate the influence of the base on the anodic potentials. The influence of electron withdrawing group, ciano group in A and nitro group in B, is considered taking 2,2-diphenyl-1-(2,4-dinitrophenyl)hydrazine (C) as reference compound. A mechanism for the three oxidation steps of compound A is proposed. Quantum chemical calculations confirmed the mechanism.



INTRODUCTION

The study of free radicals has attracted interest from chemists due to their applications in several domains. One of this is the ability of free radicals to scavenge activity of antioxidants in foods, which are health-protecting factors. The antioxidants reduce risks for some chronic diseases, like cancer and heart conditions. These substances have ability to trap free radicals present in biological systems and may oxidize proteins, lipids, nucleic acids or DNA, initiating degenerative diseases. The free radical scavenging activity of antioxidants has been investigated and reported in the literature.[1,2]

In 1922 Goldschmidt synthesized one of the most known free radical derived from hydrazine is DPPH (2,2-diphenyl-1-picrylhydrazyl).[3]

The reaction of DPPH with numerous antioxidants is widely used in plant biochemistry to evaluate the properties of plant constituents for scavenging free radicals and determination of antioxidant properties of amines, phenols, vitamins, drugs, inhibition of homolytic reactions, as standard in ESR spectroscopy.[4-10] DDPH is also a good hydrogen- or electron-abstractor and generates the corresponding reduced species DPPH-H or $DPPH^-$.[11-13]

In this paper, the electrochemical behaviour of two compounds: 2,2-diphenyl-1-(2,4-dinitro-5-cianophenyl)hydrazine (A) and 2-(4-nitrophenyl)-2-phenyl-1-(2,4-dinitrophenyl)hydrazine (B), is reported. The redox couples of these hydrazine-derivatives and their interrelations could be identified. The data obtained from cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements were correlated with quantum chemical calculations. The influence of the CN and NO_2 groups is discussed by referring to 2,2-diphenyl-1-(2,4-dinitrophenyl)hydrazine (compound C). Electrochemical studies of C together with other three similar compounds were reported in previous works.[14,15]

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EXPERIMENTAL

For voltammetric measurements, the following instrumentation was used: a potentiostat-galvanostat type Autolab PGStat 12, controlled by General Purpose Electrochemical System (GPES) with interface for Windows (version 4.9.007). The three-electrodes in one-compartment cell (10 mL) were connected to the potentiostat. As working and counter electrode two disk-shaped platinum electrodes (Metrohm, 3 mm in diameter) were used. A wire of Ag served as pseudo-reference electrode. The surface of platinum electrodes was cleaned by polishing with alumina slurry, washed with twice-distilled water and sonicated for 1 minute. The solutions were deaerated by purging with high purity argon for 15 minutes. The measurements were carried out at room temperature under a blanket of low pressure inert gas maintained above the solution.

Compounds 2,2-diphenyl-1-(2,4-dinitro-5-cianophenyl)hydrazine (A) and 2-(4-nitrophenyl)-2-phenyl-1-(2,4-dinitrophenyl)hydrazine (B), were synthesised as described in previous articles. [16,17] The other reagents were of analytical grade: acetonitrile (Fisher Chemicals), tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) (Fluka), sodium hydroxide (Sigma), methanol (Chimopar) and used without any further purification.

The working solutions of 10 mL each were prepared by dissolving the electroactive compounds A or B (1 mM) in acetonitrile with 0.1 M Bu_4NBF_4 as supporting electrolyte. The behaviour of A and B in basic medium was also studied after adding 0.1 mL NaOH 0.11 M in methanol to the former solutions. The obtained effect was the hydrogen-atom abstraction from hydrazyl moiety. CV and DPV measurements were performed in both cases.

The quantum chemical calculations were performed with the Gaussian09 program [18] using the DFT method with a B3LYP functional [19,20] and the TZVP basis set[21]. The adiabatic, E_a, energies of several possible oxidation processes of the form Red ↔ Ox + e^- were computed as E_{Ox}-E_{Red}, in order to be correlated to the experimental oxidation potential from cyclic voltammetry. These energies correspond to the optimized geometry of the respective species. The solvent, acetonitrile, was modelled as a polarizable continuum in the frame of the PCM model. [22]

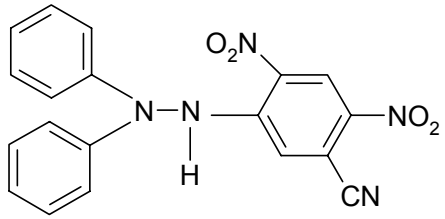
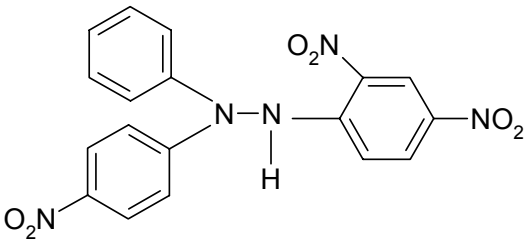
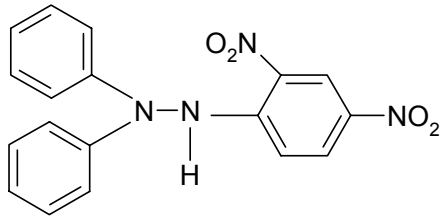
RESULTS AND DISCUSSION

The structures of the investigated compounds are presented in Table 1.

For both compounds CV and DPV experiments were carried out in the potential ranges: from -0.50 V to +1.75 V for A and , from -0.60 V to +1.55 V for B. The influence of scan rate was investigated and several values were used in the range between 0.05 to 0.75 V s^{-1}. The DPV parameters were: step potential 10 mV, and two values for modulation amplitude 25 and 50 mV, respectively.

Table 1

Structures of hydrazine derivatives

Compound	Substance name	Structure
(A)	2,2-diphenyl-1-(2,4-dinitro-5-cianophenyl)hydrazine	
(B)	2-(4-nitrophenyl)-2-phenyl-1-(2,4-dinitrophenyl)hydrazine	
(C)	2,2-diphenyl-1-(2,4-dinitrophenyl)hydrazine	

Electrochemical study of 2,2-diphenyl-1-(2,4-dinitro-5-cianophenyl)hydrazine (A)

The CV and DPV studies of compound A, in the absence of methoxide ion and in the presence of methoxide ion, at different scan rates and on different potential domains, indicate a complex redox response due to the multistep occurrence of the heterogeneous electron transfers and coupled protonation-deprotonation chemical reaction intervening in the last electron transfer. The CV study accomplished on the three different potential domains, allow to establish the genetic link between the anodic and the cathodic peaks. The first two couples of peaks are close to the reversible behaviour, while the third is an EC mechanism. A comparison of compound A redox behaviour in the two media is presented in Fig. 1, both in CV and DPV techniques. The redox behaviour is more or less the same, a cathodic shift of each peak potential is recorded in the presence of methoxide ion due probably to the preceding abstraction of proton from the N-H group by the base. In the anodic direction, in CV study the shifts are 21, 25 and 78 mV. These cathodic shifts confirm that the anodic reaction occurs easier for deprotonated species than for protonated species. Considering the shape factor (Table 2), all electron transfers are single-electron electrode reactions.

Electrochemical study of 2-(4-nitrophenyl)-2-phenyl-1-(2,4-dinitrophenyl)hydrazine (B)

The CV and DPV studies of compound B, both in the absence and in the presence of methoxide ion, confirm the multistep occurrence of the heterogeneous electron transfers and coupled protonation-deprotonation chemical reaction intervening in the last electron transfer. The presence of $-NO_2$ group in *para* position represses the heights and leads to significant shifts of the peaks.

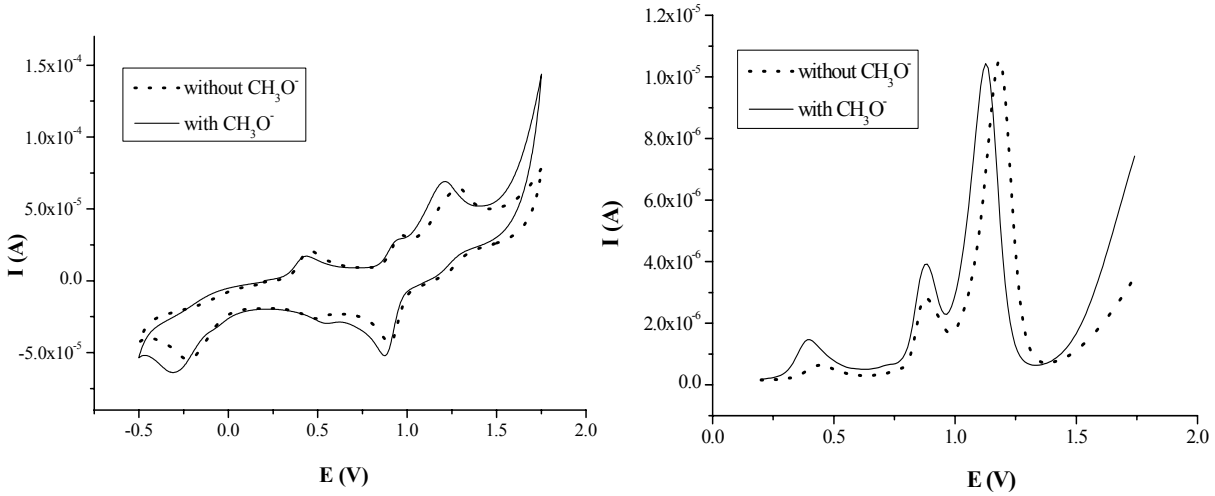


Fig. 1 – a) Cyclic voltammograms of (A) 2,2-diphenyl-1-(2,4-dinitro-5-cianophenyl)hydrazine (1 mM) in acetonitrile/Bu_4NBF_4 (0.1M) in the presence (line) and absence (dot) of methoxide ion at 0.5 V s^{-1}, b) DPV traces of A in the presence (line) and absence (dot) of methoxide ion, DPV parameters being SP=10 mV and MA=25 mV.

Table 2

Main CV data for 2,2-diphenyl-1-(2,4-dinitro-5-cianophenyl)hydrazine (A) in the absence and presence of methoxide ion at 0.5 V/s

	E_{pa1}	$E_p - E_{p/2}$	E_{pa2}	$E_p - E_{p/2}$	E_{pa3}	$E_p - E_{p/2}$
without CH_3O^-	0.452	0.063	0.957	0.050	1.279	0.106
with CH_3O^-	0.431	0.066	0.932	0.052	1.201	0.094

Influence of the ciano and nitro groups

One can consider compound C as common reference for both A and B. The presence of the electron withdrawing effect of CN group in the *meta* position in A compared to C has a little direct influence on the stability of the radical. On the whole, ciano group decreases in some extent the electronic density at N atom comparative to the electronic density corresponding to the lone pair of electrons in compound C. As a consequence, in the absence of the methoxide ion, compound A will be oxidised harder than compound C. An anodic shift is measured for the two anodic peaks for A compared to C. CV data for compound C were presented in a previous paper.[14] Regarding the third peak, a cathodic shift can be noticed (see Fig. 2).

The presence of the electron withdrawing effect of NO_2 group in the *para* position in B compared to C influences the stability of the radical. On the whole, nitro group decreases in a greater extent the electronic density at N atom comparative to the electronic density corresponding to the lone pair of electrons in compound C. As a consequence, in the absence of the methoxide ion, compound B will be oxidised even harder than compound C. In addition, the peak currents are lower.

Quantum chemical calculations

Quantum chemical calculations were performed on compounds A and B in order to explain the mechanism of the electrochemical processes. Only the non-concerted deprotonation-electron transfer processes as the first oxidation step were taken into account (as in Scheme 1). The experimental values of the oxidation potentials are considered to increase in the same order as the computed energy, E_a, of the respective adiabatic process noted as (1), (2), (3) in Scheme 1.

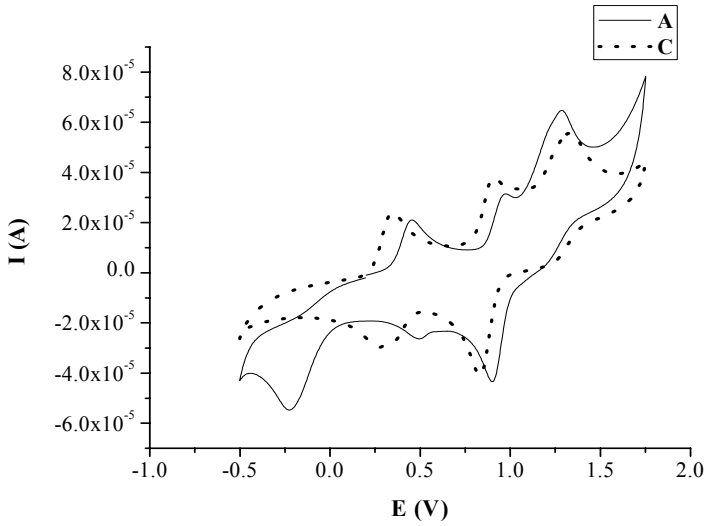
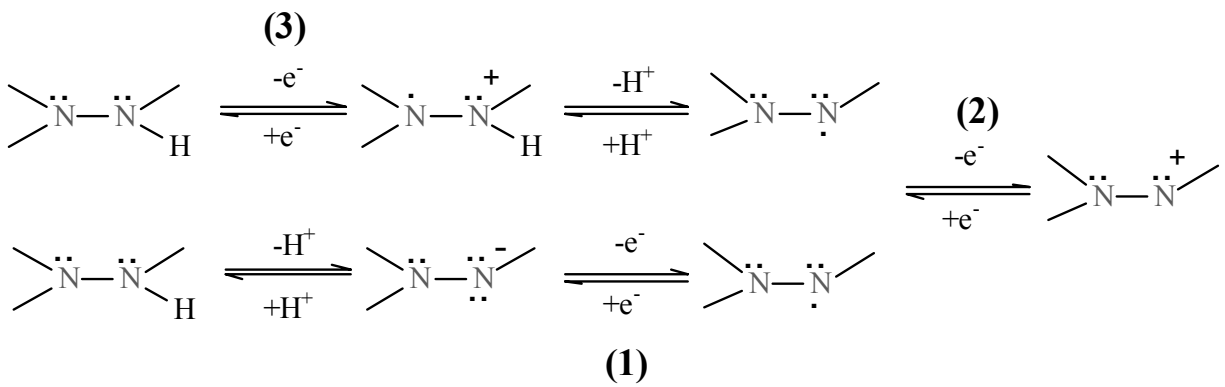


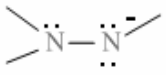
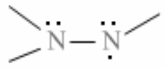
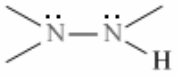
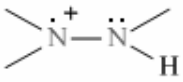
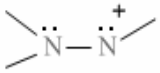
Fig. 2 – Superposition of cyclic voltammograms of compounds A (line) and C (dot), each 1 mM in acetonitrile/BU_4NBF_4 (0.1M), potential domain -0.5 --- 1.75 V, scan rate 500 mV/s.



Scheme 1 – Mechanism of the redox and acidic-basic behaviour of hydrazine moiety.

Table 3

Calculated ionisation potentials

Species	Oxidative step	E_a (eV) compound A	E_a (eV) compound B
	(1)	4.58	4.71
	(2)	5.32	5.34
	(3)	5.67	5.89
	-	6.73	6.86
	-	7.82	7.91

The oxidation process is controlled by the HOMO orbital, so at a first glance on the energy of the HOMO/SOMO orbitals depicted in Fig. 3, one can see that the oxidation takes place in the order hydrazyl anion < hydrazyl radical < hydrazine < hydrazine cation < hydrazyl cation, matching the order of the electrochemical processes in Scheme 1. Apart from contribution from the phenyl rings, all HOMO orbitals are located on one or both nitrogen atoms, showing the location of the oxidation processes on the hydrazine group. The calculated ionization potentials, E_a, are presented in Table 3.

They increase in the order (1) < (2) < (3) for both compounds A and B, confirming the mechanism assigned in Scheme 1. The oxidation process that takes place at the lower potential is that of the anionic hydrazyl to the hydrazyl radical, subsequent to the abstraction of a proton from the hydrazine molecule. This has an adiabatic ionization potential of 4.58 eV for compound A and 4.71 eV for B. The second one is that of the hydrazyl radical, with a value of 5.32 and 5.34 eV, respectively, while the third value, 5.67 and 5.89 eV, for A and B, respectively. These values were found for the oxidation of the hydrazine molecule to the hydrazine cation, which may further lose a proton to form the hydrazyl radical and should correspond to the third wave in the cyclic voltammogram, which has a very small counterpeak (EC mechanism, with the chemical step corresponding to losing the proton). As these theoretical values cannot be directly correlated to the experimental voltammetric data, it is best to correlate the difference between two consecutive of these values, which is, respectively, for compounds A and B, $E_a(2)-E_a(1)=0.74$ and 0.63 eV and $E_a(3)-E_a(2)=0.35$ and 0.55 eV. They acceptably agree with the difference between two consecutive oxidation potentials, i.e 0.505 V and 0.322 V for compound A in the absence of methoxide ion (see Table 2). The literature data available for the diphenylpicrylhydrazyl radical in acetonitrile indicate a difference of 0.515 V[23] between the waves assigned to the electrochemical steps (1) and (2).

As seen from Table 3, the further oxidation of the two cationic species takes place at energies larger by another approximately 1 and 2 eV then the oxidation step (3) of both compounds, which falls off the range of potential experimentally used. The only oxidation processes predicted to be seen in the cyclic voltammogram in the potential range of 0-2 V are the first three, denoted as 1-3.

Fig. 4 a and b depicts the total electronic charge density surface corresponding to the value of 0.35 e/Bohr^3 and the spin density isosurfaces (0.0025 e/Bohr^3) for the radicalic species of compound A. The radical has an excess electron density on the two central nitrogens and on the nitro groups (Fig. 4 a), but the excess of spin (black in Fig. 4b) is predominantly distributed only on the two nitrogens. There is a larger excess of spin on the phenyl located anti to the 2,4-dinitro-5-cyanophenyl fragment, so that the two phenyls are

not equivalent in what concerns the spin distribution. Although the nitro groups have an excess of electronic density, they show only a slight excess of spin in the case of the radical, surpassed by the nitrogens and the phenyl rings. Also, there is an alternacy in the spin distribution in the phenyl ring, where the carbon atoms have either an excess, or a deficit of spin (black and white isosurfaces, respectively). This is in agreement with the experimental findings for the diphenylpycrylhydrazyl radical.[24]

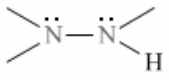
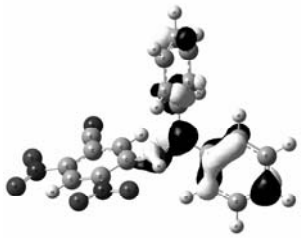
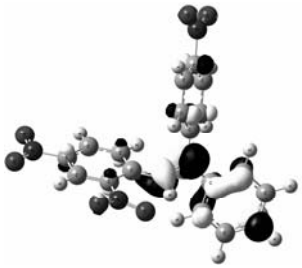
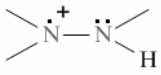
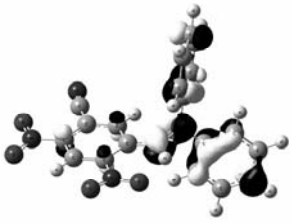
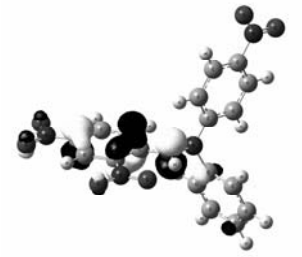
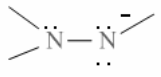
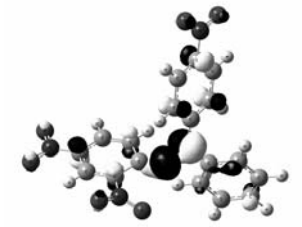
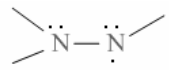
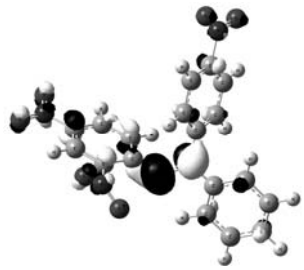
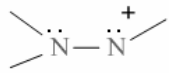
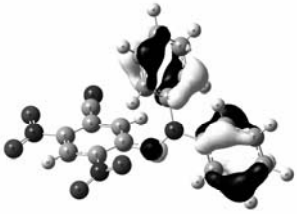
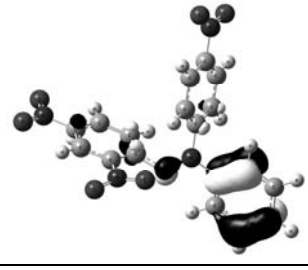
Species	Compound A	Compound B
	 -0.222	 -0.244
	 -0.258	 -0.263
	 -0.187	 -0.198
	 -0.215	 -0.217
	 -0.296	 -0.300

Fig. 3 – Isodensity surfaces (electronic density of 0.05 e/Bohr^3) for the molecular orbitals (last occupied, HOMO or SOMO) for several species of compounds A and B and their energy (in eV).

a) b)

Fig. 4 – a) Density of charge isosurface (0.35 e/Bohr^3) and b) spin density isosurfaces – black – positive; white – negative (0.0025 e/Bohr^3) for compounds A (top) and B (bottom).

CONCLUSIONS

The electrochemical (CV and DPV) behaviour of two hydrazine derivative was studied in the absence and in the presence of a hydrogen abstractor, the methoxide ion. Due to the presence of an electron withdrawing group, each compound gives rise to easier anodic reaction, but the influence of the group situated in *para* (nitro, in compound B) is more important than that of the group situated in *orto* (ciano, in compound A). The oxidation of compound A in the presence of the base occurs easier than in its absence while for compound B the first oxidation occurs harder and the last two occur easier. The DFT study accounts for the mechanism of the electrochemical oxidation of the two hydrazine derivatives.

REFERENCES

1. H. E. Miller, F. Rigelhof, L. Marquart, A. Prakash and M. Kanter, *Cereal Foods World*, **2000**, *45*, 59.
2. H. E. Miller, F. Rigelhof, L. Marquart, A. Prakash and M.Kanter, *J. Am. Coll. Nutr*., **2000**, *19*, 312.
3. S. Goldschmidt and K. Renn, *Ber.*, **1922**, *55*, 628.
4. J. S. Hogg, D. H. Lohmann and K. E Russell, *Can. J. Chem.*, **1961**, *39*, 1588.
5. M. E. Cuvelier, H. Richard and C. Berset, *Biosci. Biotech. Biochem.*, **1992**, *56*, 324.
6. M. M. Chen, K. V. Sane, R. I. Walter and J. A. Weil, *J. Phys. Chem.*, **1961**, *65*, 713.
7. O. Yukowa and T. Nakajima, *Int. J. Radiation Biol.*, **1999**, *75*, 1189.
8. J. Glavind and C. Halmer, *J. Am. Oil Chem. Soc.,* **1967**, *44*, 539.
9. M. Akitame and H. Hajime, *Neuroscience*, **1990**, *16*, 83.
10. K. Emaru, H. Askal and G. Saleb, *Talanta*, **1991**, *38*, 1219.
11. P. Ioniță, *Chem. Papers*, **2005**, *59*, 11.
12. P. Ioniță, *Free Radic. Res*, **2006**, *40*, 59.
13. P. Ioniță, *Lett. Org. Chem.*, **2008**, *5*, 42.
14. C. C. Andrei, D. Bala and C. Mihailciuc, *Rev. Roum. Chim*., **2013**, *58*, 399.
15. C. C. Andrei, L. Sărdan, S. Ionescu, D. Bala and C. Mihailciuc, *Rev. Roum. Chim*., **2014**, *59*, 645.
16. P. Ioniță, T. Constantinescu, H. Căldăraru, C. Luca, M.T. Căproiu, F. Dumitrașcu, I. Silberg and A. Balaban, *Rev. Roum. Chim*., **1999**, *44*, 393.
17. P. Ioniță, M.T. Căproiu, C. Luca, T. Constantinescu, H. Căldăraru and A. Balaban, *J. Labelled Cpd. Radiopharm.*, **1998**, *XLI*, 791.
18. Gaussian 09, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin,

V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2009**.

19. A. D. Becke, *J.Chem.Phys*., **1993**, *98*, 5648.
20. P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J.Phys.Chem*., **1994**, *98*, 11623.
21. A. Schaefer, C. Huber and R. Ahlrichs, *J. Chem. Phys*., **1994**, *100*, 5829.
22. J. Tomasi, B. Mennucci and R. Cammi, *Chem. Rev*., **2005**, *105*, 2999.
23. E. Solon, A. J. Bard, *J. Am. Chem. Soc.*, **1964**, *86*, 1926; Monatshefte fur Chemie, **1983**, *114*, 1035.
24. J. X. Boucherle, B. Gillon, J. Maruani and J. Schweizer, *Mol. Phys.*, **1987**, *60*, 1121.