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Dedicated to Professor Victor-Emanuel Sahini on the occasion of his 80th anniversary

MODELLING OF THE ELECTROCHEMICAL REDUCTION BEHAVIOUR OF SOME DIBENZ[b,e]-THIEPINONSULPHONES BY THE DFT METHOD

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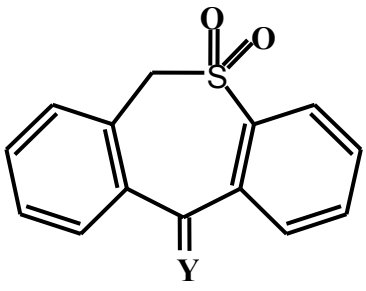
The reducibility of two sulphones in the benzothiepinone class, dibenzo[b,e]-tiepinone-5,5 dioxide (**1**) and dibenzo[b,e]-tiepin-tione-5,5 dioxide (**2**) and the cleavage reaction of the seven membered ring observed upon electrochemical reduction was studied by the DFT method. The calculations were performed on the neutral molecules and the corresponding charged species, the anion radicals and the dianions. The main feature of the reduction mechanism, the cleavage of the sulphur containing median ring, was accounted for by the shape of sections through the potential energy surfaces along the two possible reaction coordinates, the CH_2-SO_2 and $C_{aromatic}$-SO_2 bonds. The calculations are in good agreement with the previous experimental data.

INTRODUCTION

Theoretical modelling of electrochemical reactions has become an important complementary tool in the last years in monitoring the reaction mechanism and the intermediates. On the other hand, the presence of charged species in a series of biological redox processes[1-3] determines an increased attention for the good characterisation of their properties. The possibility to consider the presence of the solvent in the frame of different available solvent models at both the semiempirical and ab initio levels enhances the interest for such calculations.

The previously studied reduction process of two dibenz[b,e]-tiepinonsulphones,[1] Fig.1, revealed an interesting mechanism based upon the ring opening reaction of the central seven membered ring, [4] *i.e.* the breaking of the CH_2-SO_2 bond.

The experimental data showed that for compound **1** the ring cleavage occurs after the first heterogeneous electron transfer, the resulting anion radical (AR) being very unstable and not detected by ESR spectroscopy, whereas for compound **2**, the anion radical is stable enough to be characterised by ESR spectroscopy and to undergo a second electron transfer reaction, the ring breaking occurring from the dianion. The main steps of the mechanisms are given in Scheme 1.



(1) Y=O dibenzo[b,e]-tiepinone-5,5 dioxide;
(2) Y=S dibenzo[b,e]-tiepin-tione-5,5 dioxide;

Fig. 1 – Molecular formula of the studied compounds.

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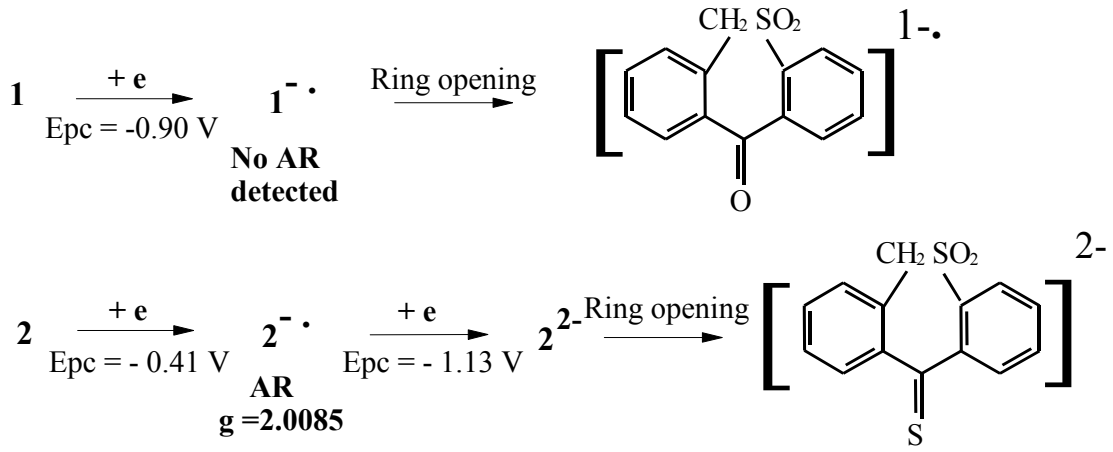

Scheme 1

The modelling of both mechanisms by the solvent-dependent PM3 method in the frame of the AMSOL program as well as by the 6-31G ab initio method supports the experimental data and allows for the estimation of the energy barriers for the ring opening reactions in the range of 4-10 kcal mol^{-1} for **1** and 6-17 kcal mol^{-1} for **2**, depending on the used method. [5]

As recent literature data show that the DFT method is more appropriate for the theoretical characterisation of charged species[6-11], the aim of this paper is a DFT study of the electrochemical processes to which the two dibenz[b,e]-tiepinonsulphones are submitted. We aim at elucidating the two mechanisms and to explain on a theoretical basis the different reactivity of the studied compounds. The following strategy was used: i) calculation of the vertical and adiabatic electron affinity for the neutral and charged species and correlation with the experimental reducibility; ii) modelling of the ring-opening reaction in order to explain the different stability of the corresponding anion-radicals.

COMPUTATIONAL METHOD

The calculations were performed by the DFT method employing the Becke3-Lee-Yang-Parr B3LYP [12] exchange correlation functional in combination with the 6-31G basis set using the Gaussian 98 program.[13] For the open- and closed-shell species the unrestricted and restricted calculation methods were used, respectively.

The geometry of all the species in the system, the neutral molecules, the anion radicals (Charge = -1; S = 1/2) and the dianions (Charge = -2, S = 0) were fully optimised and the vertical and adiabatic electron affinities (E_{ad} and E_v) and electronegativities (χ_v and χ_{ad}) were calculated using the relationships:[14-17]

$$E_v = -(E_{AR} - E_M)$$

where E_{AR} and E_M represent the energies of the anion radical and the neutral molecule at the optimised geometry of the neutral molecule;

$$E_{ad} = -(E_{AR} - E_M)$$

where E_{AR} and E_M have the same meaning but are calculated at the optimised geometry of each species;

$$\chi_v = -\ 1/2\ (\varepsilon_{HOMO} + E_v);$$

$$\chi_{ad} = 1/2\ (E_{CR} - E_M) - 1/2\ (E_{AR} - E_M),$$

where E_{CR} represents the energy of the cation radical and the other quantities have the usual meaning.

Sections through the potential energy surfaces (PES) were built maintaining a constant value for one of the internal coordinates and allowing for the full relaxation of all other coordinates; since in our case, the main problem was the cleavage of the CH_2-SO_2 bond; this was the coordinate used in the PES calculations, hereinafter noted $R_{CH2\text{-}SO2}$. The minimum points for all the species were characterized by the hess matrix values. The difference between the energy of highest and the minimum points on the PES sections was considered as an estimate of the energy barrier of the ring opening reactions.

RESULTS AND DISCUSSION

The first step of the reduction process is represented by the heterogeneous electron transfer reaction. The relevant parameters describing the

process are listed in Table 1. The theoretical data reflect the different reducibility of the two compounds in agreement with the experimental values of the cathodic peak potentials, E_{pc}= –0.41 V for **2** as compared to E_{pc} = -0.90 V for **1**.

On the basis of the experimental data[4] it was stated that the second step corresponds to a different reaction for each compound. In the case of compound **1** the second reaction corresponds to the ring opening reaction, whereas for compound **2** the stability of the anion radical was large enough to allow for its identification by ESR spectroscopy for the possibility of a second heterogeneous electron transfer at the potential E_{pc} = –0.89 V.

Table 1

Relevant experimental and theoretical data, the experimental cathodic peak potential (- Epc, V), the calculated vertical and adiabatic electron affinities (E_V and E_{ad}, eV) and electronegativities (χ_v and χ_{ad}, eV)

Compound	$-E_{pc}$	ε_{HOMO}	ε_{LUMO}	χ_v	χ_{ad}	E_v	E_{ad}	E_v in DMSO	E_{ad} in DMSO
1	0.90	-7.07	-2.72	4.16	4.72	1.25	1.45	-*	2.98
2	0.41	-6.25	-3.26	4.03	5.01	1.81	2.04	3.55	3.55

***** E_v for the anion radical of (**1**) in DMSO could not be calculated, as the convergence could not be reached.

The different stability of the anion radicals of **1** and **2** is well evidenced by the shape of the sections through the potential energy surfaces along the reaction coordinate $R_{CH2\text{-}SO2}$.

The calculations were performed for $R_{CH2\text{-}SO2}$ in the range of 1.80 – 4.50 Å and the results in vacuo are presented in Fig. 2. The relative energies were calculated in respect with the minimum energy point of the anion radicals.

The plots allow for the following observations. For the AR **1** a very small value for the activation energy, about E_a = 0,17 kcal mol^{-1} was found. The ring opening occurs very quickly, thus explaining the impossibility to experimentally detect the anion radical. The PES calculated in the presence of the solvent (inset of Fig. 2) shows that inclusion of the solvation process enhances the propensity for the ring cleavage, the steep energy decrease begins at smaller $R_{CH2\text{-}SO2}$ values.

For AR **2**, the energy barrier, although not very high, E_a = 4,47 kcal mol^{-1}, shows that the ring breaking process is not so rapid, being competitive with the second reduction process.

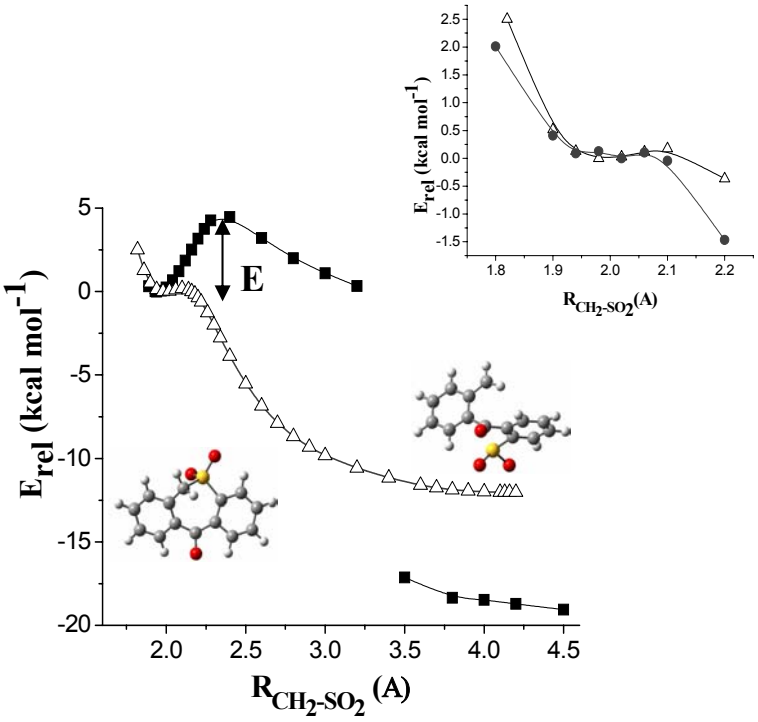

Fig. 2 – Dependence of the relative energies of the anion radicals for compounds **1** (open triangles) and **2** (filled squares) on the CH_2-SO_2 distance. (The relative energies were calculated in respect to the minimum energy point of the anion radicals). Inset: comparative plots of the relative energies for the AR **1** vs. the CH_2-SO_2 distance, in vacuo (open triangles) and in the presence of DMSO (filled circles). The geometries correspond to the anion radical of compound **1**: the optimised minimum (left) and at $R_{CH2\text{-}SO2}$=4 Å (right).

The same approach applied for the dianion of compound **2**, led to the plot in Fig. 3.

Inspection of the highest occupied molecular orbital, HOMO, in the dianion of **2** reveals an antibonding character between the CH_2 and SO_2 groups (Fig. 4); the same feature was also observed in the semiempirical and ab intio calculations and was rationalised in terms of the stepwise dissociative reduction model of Saveant, who considers that an antibonding character of a molecular orbital between two bonded atoms favours the bond cleavage.[18-20]

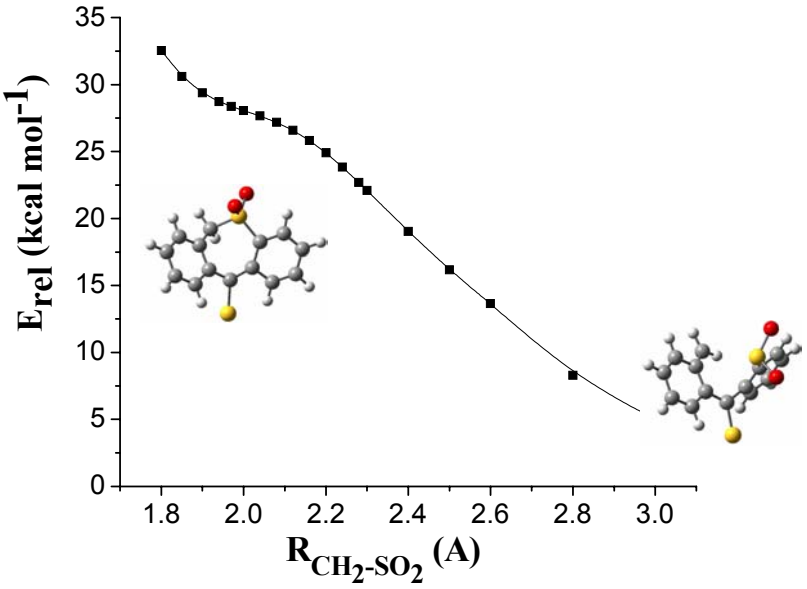

Fig. 3 – Dependence of the relative energy of the dianion of **2** on the CH_2-SO_2 distance, $R_{CH2-SO2}$. E is calculated relative to the minimum energy point found at 4 Å. The geometries correspond to the optimised minimum energy point (left) and for $R_{CH2-SO2}$=3 Å (right).

It can be seen that there is practically no energy barrier, the energy decreases steeply leading to the open form.

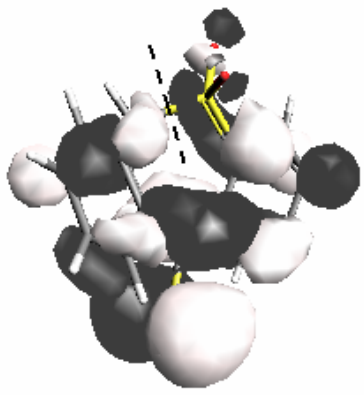

Fig. 4 – The shape of the HOMO molecular orbital for the dianion of **2**. The antibonding character at the CH_2 - SO_2 level is indicated by a dashed line.

CONCLUSIONS

The DFT calculations support the experimental results explaining the enhanced reducibility brought about by the presence of the sulphur atom and the different stability of the anion radicals. It was found that the ring opening reaction occurs starting from the anion radical for compound **1** and from the dianion for compound **2**. The presence of the solvent favours the ring opening reaction of the AR of **1**. Comparison with the previous HF calculations on the reaction systems yielded a good correlation.

REFERENCES

1. I. A. Topol, C. McGrath, E. Chertova, C. Dasenbrock, W. R. Lacourse, M. A. Eissenstat, S. K. Burt, L. E. Henderson and J. R. Casas-Finet *Protein Sci.*, **2001,** *10*, 1434-1445.
2. C. W. M. Kay, B. Mennenga, H. Gorisch, and Robert Bitt, *J. Biol. Chem*., **2006**, *281*, 1470–1476.
3. R. F. Rakowski, S. Kaya and J. Fonseca, *J Comput. Electron*., **2005**, *4*, 189–193.
4. M. Ciureanu, M. Hillebrand and E. Volanschi, *J. Electroanal. Chem.*, **1992**, *322,* 221-232.
5. E. Volanschi, S-H Suh and M. Hillebrand, *J. Electroanal. Chem.*, **2007,** in press.
6. X. Li, Z.Cai and M.D. Sevilla, *J. Phys. Chem. A*, **2002**, *106*, 1590-1604.

7. J. E. Lee, W. Choi and B. J. Mhin, *Bull. Korean Chem. Soc*., **2003**, *24*, 792-796.
8. G. N. Merrill, G. D. Dahlke, and S. R. Kass, *J. Am. Chem. Soc.*, **1996**, *118,* 4462-4468.
9. W. Bors, C. Michel, K. Stettmaier, S. P. Kazazi and Leo Klasinc, *Croat. Chem. Acta*, **2002**, *75***,** 957-964.
10. K. M. P.Bandaranayake, R. Wang and G. Hastings, *Biochemistry*, **2006,** *45,* 4121-4127.
11. A. J. Gianola, T. Ichino, R. L. Hoenigman, S. Kato, V. M. Bierbaum and W. C. Lineberger, *J. Phys. Chem. A*, **2004,** *108,* 10326-10335.
12. A. D. Becke, *J. Chem. Phys.*, **1993**, *98*, 5648-5652.
13. *Gaussian 98 (Revision A.9)*, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, P. Salvador, J. J. Dannenberg, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 2001.
14. Li Xifeng, L. Sanche and M. D. Sevilla, *J. Phys. Chem. A*, **2002**, *106*, 11248-11253.
15. D. J. Tozer and F. De Proft, *J. Phys. Chem.* A, **2005**, *109*, 8923-8929.
16. S. Ma, X. Zhang, H. Xu, L. Shen, X. Zhang, Q. Zhang, *J. Photochem. Photobiol. A*, **2001**, *139*, 97-104**.**
17. J. C. Cramer, " Essentials of Computational Chemistry", John Wiley & Sons Ltd, 2002.
18. J. M. Saveant, *Accounts Chem. Res.*, **1993,** *6*, 455-462.
19. J. F. Bergamini, P. Hapiot, C. Lagrost, L. Preda, J. Simonet and E. Volanschi, *Chem.Phys.*, **2003**, *5*, 4846-4850.
20. A. Belen Meneses, S. Antonello, M. C. Arevalo and F. Maran, *Electrochimica Acta*, **2005**, *50*, 1207-1215.