

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy



journal homepage: www.elsevier.com/locate/saa

Quantum chemical simulations of solvent influence on UV–vis spectra and orbital shapes of azoderivatives of diphenylpropane-1,3-dione

W. Kuznik^a, I.V. Kityk^{b,*}, M.N. Kopylovich^c, K.T. Mahmudov^c, K. Ozga^d, G. Lakshminarayana^e, A.J.L. Pombeiro^{c,**}

^a Department of Physical Chemistry and Technology of Polymers, Silesian University of Technology, Gliwice, Poland

^b Electrical Engineering Department, Czestochowa University of Technology, Av. Armii Krajowej 17/19, PL-42200 Czestochowa, Poland

^c Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, TU Lisbon, Av. Rovisco Pais, 1049–001 Lisbon, Portugal

^d Czestochowa University of Technology, Armii Krajowej Av. 36B, 42200 Czestochowa, Poland

e Department of Materials Science – WW3, University of Erlangen-Nuremberg, Erlangen 91058, Germany

ARTICLE INFO

Article history: Received 1 December 2010 Accepted 28 December 2010

Keywords: Azoderivatives of β-diketones Solvatochromic effect Tautomers DFT calculations

ABSTRACT

The DFT modeling of novel synthesized azoderivatives of β -diketones – 2-(2-(2-hydroxyphenyl)hydrazono)-1,3-diphenylpropane-1,3-dione (1), 2-(2-(2-hydroxy-4-nitrophenyl)hydrazono)-1,3-diphenylpropane-1,3-dione (2), 3-(2-(1,3-dioxo-1,3-diphenylpropan-2-ylidene)hydrazinyl)-2-hydroxy-5nitrobenzene sulfonic acid (3), 2-(2-(1,3-dioxo-1,3-diphenylpropan-2-ylidene)hydrazinyl)benzenesulfonic acid (4), 2-(2-(1,3-dioxo-1,3-diphenylpropan -2-ylidene)hydrazinyl)benzoic acid (5), 2-(2-(2-hydroxy-4-nitrophenyl)hydrazono)-1-phenylbutane-1,3-dione (6) were performed. The collected information confirms that 1–5 exist in hydrazo form, being stabilized by the intramolecular hydrogen bonds in DMSO solution and solid phase, while 6 exists in mixed enol-azo and hydrazo tautomeric forms, the latter dominating in more polar solvents. The relative stability of various tautomeric and izomeric forms of the symmetric 1–5 and unsymmetric 6 azoderivatives of β -diketones is calculated based on the density functional theory (DFT). Polarizable Continuum Model was used to simulate solvatochromic effects. Solvents of different polarities were used to collect experimental spectra, and the same solvents were chosen for the PCM calculations. The optical properties of 1–6 have been investigated by density functional theory (TD-DFT).

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

The search for new materials in which low-energy external effects can significantly change the overall behavior, for example their optical (including solvatochromic) properties, conductivity, electrochemical potentials etc. is a subject of the extensive theoretical and experimental investigations in the recent decades [1–3]. The strategy used to design the substances with the desired properties usually involves combination, within the same molecule, donor and acceptor groups at the terminal positions of a π -bridge to create polarized motif which is highly sensitive to the subtle external influences and can also exhibit some nonlinear properties [4–7].

In the search of new motifs possessing such properties we have found that azoderivatives of β -diketones (ADB) are good potential candidates. Theoretically ADB can exist in three tautomeric

forms (enol-azo, keto-azo and hydrazo) [8-13] with conjugated donor- π -acceptor motif, which already made them promising candidates for such applications as bistate molecular switches [14–21], optical recording media and spin-coating films [22,23] or photoluminescent [24] materials. In our recent work [11] we have found that ADB containing a hydroxyl group in ortho-position to the hydrazo group and formed from the *unsymmetrical* β-diketones, exist in solution in two distinct tautomeric forms namely enol-azo and hydrazo-, and that a ratio between these forms depends on the solvent used as well as on temperature. On the other hand, it was shown that in the solid state these ADB compounds are stabilized only in hydrazo form [11]. It was assumed that the tautomers in solution are stabilized by a strong intramolecular resonance assisted hydrogen bond (RAHB), and that the tautomeric balance can play an important role for many applications involving subtle transitions [14-21].

Thus, we decided to extend this study towards detailed investigation of solvatochromic properties of the other newly synthesized ADB, namely 2-(2-(2-hydroxyphenyl) hydrazono)-1,3-diphenylpropane-1,3-dione (**1**), 2-(2-(2-hydroxy-4-nitrophenyl)hydrazono)-1,3-diphenyl propane-1,3-dione (**2**),

^{*} Corresponding author. Tel.: +48 601 50 42 68; fax: +48 34 3250 821.

^{**} Corresponding author. Tel.: +351 218419237; fax: +351 21846445.

E-mail addresses: ikityk@el.pcz.czest.pl (I.V. Kityk), pombeiro@ist.utl.pt (A.J.L. Pombeiro).

^{1386-1425/\$ –} see front matter s 2010 Elsevier B.V. All rights reserved. doi:10.1016/j.saa.2010.12.080

| $\begin{bmatrix} R_1 & R_3 \\ C = 0 & H & L \end{bmatrix}$ | 1-6 | R ₁ | R ₂ | R ₃ | R ₄ | R ₅ | R ₆ |
|--|-----|-------------------------------|-------------------------------|-------------------|-------------------|-----------------|-----------------|
| | 1 | C ₆ H ₅ | C ₆ H ₅ | ОН | Н | Н | Н |
| | 2 | C ₆ H ₅ | C ₆ H ₅ | OH | Н | NO ₂ | Н |
| ^R 2 R ₆ | 3 | C ₆ H ₅ | C ₆ H ₅ | OH | SO ₃ H | Н | NO ₂ |
| | 4 | C ₆ H ₅ | C ₆ H ₅ | SO ₃ H | Н | Н | Н |
| | 5 | C ₆ H ₅ | C ₆ H ₅ | СООН | Н | Н | Н |
| | 6 | CH ₃ | C ₆ H ₅ | OH | Н | NO ₂ | Н |

Scheme 1. Azoderivatives of β-diketones considered in this work.

3-(2-(1,3-dioxo-1,3-diphenylpropan-2-ylidene)hydrazinyl)-2-hydroxy-5-nitrobenzenesulfonic acid (**3**), 2-(2-(1,3-dioxo-1, 3-diphenylpropan-2-ylidene)hydrazinyl) benzenesulfonic acid (**4**), 2-(2-(1,3-dioxo-1,3-diphenylpropan-2-ylidene)hydrazinyl)

benzoic acid (**5**), 2-(2-(2-hydroxy-4-nitrophenyl)hydrazono)-1-phenylbutane-1,3-dione (**6**). As can be seen (Scheme 1), these compounds offer better π -electron delocalization across the donor-acceptor links (enol-azo \rightleftharpoons hydrazo transition) in comparison to the ones studied by us before [11]. Substitutions at the β -diketone fragment and aromatic part of molecule have been made to ensure that the ADB indeed acts as a π -conjugated backbone. Various aromatic donors and acceptors have been used to cover a wide representation of the ADB group.

2. Experimental

2.1. Equipment and materials

The ¹H and ¹³C NMR spectra were recorded at room temperature on a Bruker Avance II + 300 (UltraShieldTM Magnet) spectrometer operating at 300.130 and 75.468 MHz for proton, and carbon-13, respectively. The chemical shifts are reported in ppm using tetramethylsilane as an internal reference. The infrared spectrum (4000–400 cm⁻¹) was recorded on a Nicolet FT-IR Nexus spectrophotometer using KBr pellets. Carbon, hydrogen, and nitrogen elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico.

UV-vis spectra were recorded in methanol, acetonitrile, dichloromethane and n-hexane (HPLC grade) solutions (concentrations approximately 50 mg/L) in standard 1 cm path length quartz cell using HP 8452A UV-vis Diode Array Spectrophotometer in the range 190–820 nm with spectral resolution 2 nm.

Cyclic voltammetry measurements were performed on AUTOLAB PGSTAT20 potentiostat–galvanostat (EcoChemie, Netherlands). Platinum wire (ϕ = 1 mm) with a working area of approximately 0.10 cm² was used as a working electrode. Silver wire was used as a quasi-reference electrode, while platinum coil served as an auxiliary one. Silver quasi-reference electrode's potential was calibrated using ferrocene as an internal standard. The electrolyte solution used was 0.2 M Bu₄NPF₆ (Aldrich 98% pure) in acetonitrile (POCh 99.8% HPLC grade). Prior to the measurements the solution was purged with argon to remove residual oxygen. As the ferrocene redox pair potential with respect to free electron in vacuum at rest is known [25–27] oxidation and reduction potentials with respect to the ferrocene redox pair were recalculated to HOMO and LUMO energy levels.

2.2. Calculation procedure

All the DFT calculations were performed using GAUSSIAN09 [28]. GABEDIT 2.2.8 Graphical User Interface [29] was used to generate input files and to produce graphs from output files. The calculations were performed at 6-31G (d) DFT B3LYP level with PCM (Polarizable Continuum Model) [30–33] applied to simulate solvatochromism. Time-dependent density functional theory (TD-DFT) was used to simulate UV–vis absorption spectra.

2.3. Synthesis of the azoderivatives of β -diketones

The compounds were prepared via the Japp–Klingemann reaction [34–36] involving diazotization of aromatic amines with following azocoupling of thus formed diazonium salt and β diketones in water solution containing sodium hydroxide [12,37].

2.3.1. Diazotization

A 0.025 mol portion of substituted aniline was dissolved in 50 mL of water and then 1.00 g of crystalline NaOH was added. The solution was cooled in an ice bath to 273 K and then 1.725 g (0.025 mol) of NaNO₂ was added; after that 5.00 mL (33%) HCl was added in portions for 1 h. The temperature of the mixture should not exceed 278 K. The resulting diazonium solution was used directly in the following coupling procedure.

2.3.2. Azocoupling

1.00 g (0.025 mol) of NaOH was added to a mixture of 0.025 mol of β -diketone with 50 mL of water–ethanol (1:1, v/v). The solution was cooled in an ice bath to *ca*. 273 K, and a suspension of 4-substituted diazonium (see above) was added in three portions under vigorous stirring for 1 h.

The identity of 1-6 was demonstrated by element analysis, IR and ¹H and ¹³C NMR spectrometry (for details see Supporting Information).

3. Results and discussion

3.1. Synthesis of **1–6** and spectroscopic study

Usually ADB are synthesized by diazotization of aromatic amines and coupling of thus formed diazonium salt with β diketone in the presence of sodium acetate (synthetic procedure commonly known as a Japp–Klingemann reaction). However, in our case this method gives a low yield of a highly impure product. Therefore, we have modified the synthesis and used sodium hydroxide instead of sodium acetate to get β -diketone carboan-



Scheme 2. Possible tautomeric equilibria for 6.

ion [12,37], that allowed us to get good yields of considerably pure compounds.

The ¹H NMR spectra of **1–5** prepared from *symmetrical* 1,3diphenylpropane-1,3-dione show only one set of signals for each compound in DMSO, where the broad signal at $\simeq ca$. 13.2–14.1 can be assigned to =N–N<u>H</u> adjacent to the aryl unit similarly to the reported analogs [8–13,37–42]. Moreover, the presence of two C=O resonances in ¹³C{¹H} NMR spectra in the range of 185.36–195.72 and a single C=N resonance at *ca*. 133.4–136.5 indicates that **1–5** exist in solution in the hydrazo form. In the solid state their IR spectra reveal the presence of NH, C=O, C=O···H and C=N vibration at *ca*. 2927–3448, 1684–1635, 1596–1623 and 1501–1596 cm⁻¹, correspondingly, indicating that **1–5** are stabilized in the H-bonded hydrazone forms.

On the other hand, ¹H NMR spectrum of **6** formed from *unsymmetric* 1-phenylbutane-1,3-dione in MeOD- d^4 and DMSO- d^6 at room temperature consists of two sets of signals, indicating that in these solvents the compound exists as a mixture of two tautomeric forms – enol-azo and hydrazo (Scheme 2) [11]. With an increase in the polarity of solvents (MeOD < DMSO) the tautomeric balance shifts to the hydrazo form (86% enol-azo, 14% hydrazo in

MeOD and 78% enol-azo, 22% hydrazo in DMSO). The third tautomeric form, viz. keto-azo, was not detected in solution under any experimental conditions, presumably due to its lower stability in comparison with the others. Hence, using those data, one can predict and tune the tautomeric equilibrium in the appropriate solvent. Although **6** was proved to exist in solution as a mixture of two tautomeric forms, IR spectrum (ν (NH) and ν (C=N) vibrations at 3184 and 1527 cm⁻¹, respectively) shows that in the solid state it is stabilized in the hydrazo form (Scheme 2) similarly to the reported analog [11].

3.2. Cyclic voltammetry

HOMO and LUMO levels are summarized in Table 1. As oxidation is a withdrawal of an electron from the studied molecule, it informs one about the energy level of the electron, which is the most easily available, that is the one described by HOMO orbital. The oxidation potential is read from the graph and translated into an absolute scale by multiplying by (-1) and adding 5.064 [43,44] to yield HOMO energy level with respect to vacuum. LUMO level is determined from the reduction peak using analogous procedure. 57

5.5

52

| HOMO and LUMO levels and energy gaps determined by the cyclic voltammetry. | | | | | | |
|--|----------|----------|--|--|--|--|
| 1–6 | HOMO [V] | LUMO [V] | | | | |
| 1 | 3.5 | 5.5 | | | | |
| 2 | 3.1 | 5.7 | | | | |
| 3 | 3.2 | 5.4 | | | | |

| 3.3. | DFT | calcu | lations |
|------|-----|-------|---------|
| | | | |

All the geometry optimization jobs converged to hydrazo form regardless the polarity of solvent simulated by PCM, even if enolazo form was used as an initial geometry (Fig. 1). A clear correlation between molecules' dipole moment and solvent polarity can be seen in the calculation results (Table 2). The dipole moment generally increases with increasing solvent polarity, 2 being the only

31

3.1

35



Fig. 1. Initial, final and one of the intermediate geometries of 1 in a DFT geometry optimization. The final, energetically preferable geometry is the hydrazo form.

exception. The procedure to generate the absorption spectra was as follows: first the geometry was optimized by the DFT method with or without PCM, and then a TDDFT calculation was performed using the previously obtained geometries.

Energy gap [nm]

628

472

584

475

522

715

Energy gap [eV]

2.0

2.6

2.2

2.6

2.4

1.7

Table 2 presents the static dipole moments of the DFT optimized molecules. As can be seen, the functional groups included into the β-diketone fragment and aromatic part of the molecules influences the LUMO levels and energy gap. Besides, the energy gap of symmetrical ADB (1-5) is higher than that for the unsymmetrical one (6).

3.4. UV-vis absorption spectra

The experimental and theoretical UV-vis absorption spectra are depicted in Figs. 2-7. All the plots are charted according to the same scheme: top panel: DFT-derived spectra, bottom panel: experiments, grey line: no PCM used, black solid, dashed and dotted line: data in acetonitrile, dichloromethane and n-hexane, respectively. As it is a considerable amount of data (over forty curves altogether). it will be commented in two separate sections: first focusing on TDDFT alone, and second on solvatochromism and performance of PCM model in properly addressing it.

3.4.1. Experimental data and the TDDFT simulations

In general, time-dependent DFT prediction (grey line, top panel) is a good approximation of the absorption spectra of the studied azo compounds. Even though the first peak is shifted approximately 40 nm to the red, which is a well known drawback of the DFT method, all the main peaks are correctly simulated. In most of the studied cases the relative peak intensities were adequately described by the theoretical prediction, and correspondence with experimental data is especially good for 4 (Fig. 5).

3.4.2. Solvatochromism and the CPM model performance

All the theoretical simulations show strong dependence on the solvent chosen for the PCM calculation, except from 4, which is only weakly correlated with solvent type used. Generally, the more polar the solvent, the stronger batochromic shift which is clearly visible especially in the violet to green range of the spectra. As this area is of the greatest interest to practical applications, we will concentrate on this part of the spectrum and only shortly comment on the ultraviolet range. Theoretical prediction of the UV part of the spectrum is highly satisfactory and accurate and it proves TDDFT potential to be used in optically active material research. The absence of any peak below 230 nm in dichloromethane solutions is merely a result of light absorption by the solvent itself.

The visible region of the spectra, on the other hand, is more interesting and posed quite a challenge to the DFT methods to predict. It is probably due to the ability of these compounds to be present in many different forms (Scheme 2). Also, the electrons can be highly delocalized in these conjugated systems. For all the cases except from **4** the peak lowest in energy is highly dependent upon the solvent used in calculation, and the difference between n-hexane (the least polar) and acetonitrile (the most polar) is approximately 30 nm. When looking at the 1 and 3 plots (Figs. 2 and 4) it would seem that all the PCM-including calculations failed to compare the

4

5

6

| Static dipole moments of DFT optimized molecules. | | | | | | | |
|---|------|------|------|------|--|--|--|
| Dipole moment [Debye] | 1 | 2 | 3 | 4 | | | |
| Acetonitrile | 6.77 | 3.31 | 5.69 | 4.59 | | | |
| Ethanol | 6.76 | 3.32 | 5.69 | 4.57 | | | |
| Dichloromethane | 6.41 | 3.33 | 5.17 | 4.17 | | | |
| n-Hexane | 5.28 | 4.86 | 5.09 | 2.91 | | | |
| No PCM used | 4.01 | 4.49 | 4.45 | 2.45 | | | |

Table 2

"ordinary" TDDFT - they show very strong solvatochromism, which cannot be seen in the experimental spectra. However, a closer look at 2, 5 and 6 reveals an interesting result. When the substance is in polar solvent, a new peak emerges about 40 nm to the red from the next peak, and the peaks relative intensity rises with solvent polarity - it is higher in acetonitrile than in dichloromethane, and the peak is absent from spectra measured in n-hexane. We believe it is precisely the peak TDDFT simulation with PCM model predicted. It

5

5.79

5.78

5.4

427

3.66



Fig. 2. UV-vis absorption spectra of 1. Top panel: spectra predicted by 6-31G(d) BLYP DFT with or without PCM; bottom panel: experimental spectra, approx. 50 mg/L. ACN - acetonitrile, DCM - dichloromethane, and nHEX - n-hexane.



Fig. 3. UV-vis absorption spectra of 2. Top panel: spectra predicted by 6-31G(d) BLYP DFT with or without PCM; bottom panel: experimental spectra, approx. 50 mg/L. ACN - acetonitrile, DCM - dichloromethane, and nHEX - n-hexane.

6

9.19

9.18

8.9

7.84

7.05



Fig. 4. UV-vis absorption spectra of 3. Top panel: spectra predicted by 6-31G(d) BLYP DFT with or without PCM; bottom panel: experimental spectra, approx. 50 mg/L. ACN – acetonitrile, DCM – dichloromethane, and nHEX – n-hexane.



Fig. 5. UV-vis absorption spectra of 4. Top panel: spectra predicted by 6-31G(d) BLYP DFT with or without PCM; bottom panel: experimental spectra, approx. 50 mg/L. ACN - acetonitrile, DCM - dichloromethane, and nHEX - n-hexane.

| Fxcited | states | of 2 | 5 | and (| 5 |
|---------|--------|-------|---|-------|----|
| LACITU | states | 01 4, | | anu | э. |

| First excited states | Acetonitrile | | | Dichloromethane | | | n-Hexane | | |
|----------------------|----------------|-------------|------------------------|-----------------|-------------|------------------------|-----------------|-------------|------------------------|
| | Energy [eV] | Energy [nm] | Oscillator strength | Energy [eV] | Energy [nm] | Oscillator strength | Energy [eV] | Energy [nm] | Oscillator strength |
| 2 | 2.654 | 467 435 | 0.8776 | 2.688 | 462 435 | 0.7593 | 2 876 | 431 | 0 8742 |
| 5 | 2.989 3.091 | 415 401 | 0.708 0.0935 | 3.019 3.087 | 411 402 | 0.5778 0.1928 | 3.034 3.17 | 409 391 | 0.0212 0.6286 |
| 6 | 2.64 2.932 | 470 432 | 0.9734 0.0717 | 2.6788 2.93 | 463 423 | 0.9207 0.0985 | 2.797 2.9534 | 443 420 | 0.4901 0.0024 |



Fig. 6. UV-vis absorption spectra of 5. Top panel: spectra predicted by 6-31G(d) BLYP DFT with or without PCM; bottom panel: experimental spectra, approx. 50 mg/L. ACN - acetonitrile, DCM - dichloromethane, and nHEX - n-hexane.



Fig. 7. UV-vis absorption spectra of 6. Top panel: spectra predicted by 6-31G(d) BLYP DFT with or without PCM; bottom panel: experimental spectra, approx. 50 mg/L. ACN – acetonitrile, DCM – dichloromethane, and nHEX – n-hexane.

seems that the excited states are affected by polar solvents and the PCM model predicted it in all the cases, but in reality it took place only in **2**, **5** and **6**. The first excited states in the predicted spectra are strongest in polar solvents (Table 3), in n-hexane they are either weak (**6**), negligibly small (**5**) or completely absent (**2**). Apparently these molecules, when placed in polar solvents, can absorb photons of two different energies: one predicted by the PCM model, and the other one by TDDFT with no PCM used. Thus, to properly predict those spectra both these calculations must be taken into account. Neither of the two calculation procedures was able to predict the whole spectrum (namely both peaks in the visible range), probably because calculations are limited to only one molecule conforma-

tion/excitation, while numerous different conformations coexist in real solutions.

4. Conclusions

In this work we present time-dependent density functional theory approach to investigate the UV-vis spectra of new organic compounds: azoderivatives of β -diketones – 2-(2-(2-hydroxyphenyl)hydrazono)-1,3-diphenylpropane-1,3-dione (1), 2-(2-(2-hydroxy-4-nitrophenyl)hydrazono)-1,3-diphenylpropane-1,3-dione (2), 3-(2-(1,3-dioxo-1,3-diphenylpropan -2-ylidene)hydrazinyl)-2-hydroxy-5-nitrobenzenesulfonic acid

(**3**), 2-(2-(1,3-dioxo-1,3-diphenylpropan-2-ylidene)hydrazinyl) benzenesulfonic acid (**4**), 2-(2-(1,3-dioxo-1,3-diphenylpropan -2-ylidene)hydrazinyl)benzoic acid (**5**), 2-(2-(2-hydroxy-4-nitrophenyl)hydrazono)-1-phenylbutane-1,3-dione (**6**). Polarizable Continuum Model was used to simulate solvatochromic effects.

Solvents of different polarities were used to collect experimental spectra, and the same solvents were chosen for the PCM calculations. It was found that the dipole moment and absorption spectra are both dependent on solvent type and PCM calculations may predict those changes, however for most of these compounds they must be compared with "ordinary" TDDFT to obtain proper description. Incorporation of the solvent influence model into the calculations significantly changed the resultant theoretical absorption spectra. The spectral peak positions were shifted towards red wavelength in solvent-related calculations with respect to "solvent-free" TDDFT, and the shift was found to be proportional to solvent polarity. In the case of acetonitrile (the most polar of the solvents studied) this shift was as large as 40 nm. Additionally, in the experimental spectra there were some peaks present in polar solvents that were absent for non-polar solutions' spectra. These differences could be analyzed by comparison with the theoretical spectra. It was shown that certain excited states (represented by the above mentioned peaks) had vanishingly low or even zero oscillation strength when non-polar solvents were used in the calculation with respect to polar ones. It is thus recommended to employ PCM model to absorption spectra simulation of azoderivatives in various solvents.

Acknowledgments

This work has been partially supported by the Foundation for Science and Technology (FCT), Portugal, and its PPCDT (FEDER funded) and "Science 2007" programs. M.N.K. and K.T.M. express gratitude to the FCT for a post-doc fellowship and a working contract. The authors gratefully acknowledge the Portuguese NMR Network (IST-UTL Center) for the NMR facility. Calculations have been carried out in Wroclaw Center for Networking and Supercomputing (http://www.wcss.wroc.pl), grant No. 135. We would like to thank Prof. Jerzy Żak and PhD Wojciech Domagała for their valuable comments on the electrochemical measurements.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.saa.2010.12.080.

References

- M. Czerwinski, J. Bieleninik, J. Napieralski, I.V. Kityk, J.R.I. Kasperczyk Mervinskii, Eur. Polym. J. 33 (1997) 1441–1447.
- [2] M.G. Brik, E. Gondek, T. Uchacz, P. Szlachcic, P. Jarosz, K.J. Plucinski, Chem. Phys. 370 (2010) 194–200.
- [3] D.R. Kanis, M. Ratner, T.J. Marks, Chem. Rev. 94 (1994) 193-201.
- [4] P. Calaminici, K. Jug, A.M. Koester, C. Arbez-Gindre, C.G. Screttas, J. Comput. Chem. 23 (2002) 291–297.
- [5] J.L. Brédas, D. Beljonne, V. Coropceanu, J. Cornil, Chem. Rev. 104 (2004) 4971–5003.
- [6] S.A. Locknar, L.A. Peteanu, Z.G. Shuai, J. Phys. Chem. A 103 (1999) 2184– 2196.

- [7] N. Terkia-Derdra, R. Andreu, M. Sallé, E. Levillain, J. Orduna, J. Garin, et al., Chem. A Eur. J. 6 (2000) 1199–1223.
- [8] A.M. Maharramov, R.A. Aliyeva, I.A. Aliyev, F.G. Pashaev, A.G. Gasanov, S.I. Azimova, R.K. Askerov, A.V. Kurbanov, K.T. Mahmudov, Dyes Pigments 85 (2010) 1–6.
- [9] K.T. Mahmudov, M.N. Kopylovich, M.F.C. Guedes da Silva, P.J. Figiel, Y.A. Karabach, A.J.L. Pombeiro, J. Mol. Catal. A: Chem. 318 (2010) 44–50.
- [10] K.T. Mahmudov, A.M. Maharramov, R.A. Aliyeva, I.A. Aliyev, M.N. Kopylovich, A.J.L. Pombeiro, Anal. Lett. 43 (2010) 2923–2938.
- [11] M.N. Kopylovich, K.T. Mahmudov, M.F.C. Guedes da Silva, M.L. Kuznetsov, P.J. Figiel, Y.A. Karabach, K.V. Luzyanin, A.J.L. Pombeiro, Inorg. Chem., 50 (2011), doi:10.1021/ic101516k.
- [12] M.N. Kopylovich, K.T. Mahmudov, M.F.C. Guedes da Silva, L.M.D.R.S. Martins, M.L. Kuznetsov, T.F.S. Silva, A.J.L. Pombeiro, J. Phys. Org. Chem., 24 (2011), doi:10.1002/poc.1824.
- [13] A.M. Maharramov, R.A. Aliyeva, K.T. Mahmudov, A.V. Kurbanov, R.K. Askerov, Rus. J. Coord. Chem. 35 (2009) 704.
- [14] P. Gilli, L. Pretto, V. Bertolasi, G. Gilli, Acc. Chem. Res. 42 (2009) 33-44.
- [15] V. Bertolasi, V. Ferretti, P. Gilli, G. Gilli, Y.M. Issa, O.E. Sherif, J. Chem. Soc. Perkin Trans. 2 (1993) 2223–2228.
- [16] V. Bertolasi, P. Gilli, V. Ferretti, G. Gilli, K. Vaughan, New J. Chem. 23 (1999) 1261–1267.
- [17] P. Gilli, V. Bertolasi, L. Pretto, A. Lycka, G. Gilli, J. Am. Chem. Soc. 124 (2002) 13554–13567.
- [18] V. Bertolasi, L. Pretto, G. Gilli, P. Gilli, Acta Crystallogr. B 62 (2006) 850-863.
- [19] P. Gilli, V. Bertolasi, L. Pretto, G. Gilli, J. Mol. Struct. 790 (2006) 40-49.
- [20] P. Simunek, V. Bertolasi, V. Machacek, J. Mol. Struct. 642 (2002) 41-51.
- [21] J. McVie, D. Alastair, R.S. Sinclair, T.G. Truscott, J. Chem. Soc. Perkin Trans. 2 (1980) 286–290.
- [22] F. Huang, Y. Wu, D. Gu, F. Gan, Thin Solid Films 483 (2005) 251-256.
- [23] Z. Chen, F. Huang, Y. Wu, D. Gu, F. Gan, Inorg. Chem. Commun. 9 (2006) 21–24.
- [24] J. Sokolnicki, J. Legendziewicz, W. Amirkhanov, V. Ovchinnikov, L. Macalik, Hanuza, J. Spectrochim. Acta A 55 (1999) 349–367.
- M.A.N.D.A. Lemos, A.J.L. Pombeiro, J. Organometal. Chem. 332 (1987) C17–C20.
 A. Venâncio, M.F.C. Guedes da Silva, L.M.D.R.S. Martins, J.J.R. Fraústo da Silva,
- A.J.L. Pombeiro, Organometallics 24 (2005) 4654–4665.
- [27] A.J.L. Pombeiro, Eur. J. Inorg. Chem. 11 (2007) 1473–1482.
- [28] 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, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian 09, Revision A.02, Gaussian, Inc., Wallingford, CT, 2009.
- [29] A.R. Allouche, Gabedit is a Free Graphical User Interface for Computational Chemistry Packages. It is available from http://gabedit.sourceforge.net/.
- [30] S. Miertus, E. Scrocco, J. Tomasi, Chem. Phys. 55 (1981) 117-129.
- [31] S. Miertus, J. Tomasi, Chem. Phys. 65 (1982) 239-245.
- [32] A.A. Granovskt, PC GAMESS Version 7.1.E (Firefly), Copyright (c) 1994, Moscow State University, Moscow, Russia, 2008.
- [33] M.W. Schmidt, K.K. Balridge, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.H. Jensen, S. Koseki, K.A. Matsunaga, S.J. Nguen, T.L. Su, M. Windus, J.A. Dupuis, Montgomery, J. Comput. Chem. 14 (1993) 1347–1363 (PCGAMESS is partially based on GAMESS (US) ver. 6 June 1999, Iowa State Univ).
- [34] F.R. Japp, F. Klingemann, Liebigs Annalen der Chemie 247 (1988) 190-225.
- [35] H.C. Yao, P. Resnick, J. Am. Chem. Soc. 84 (1962) 3514-3517.
- [36] H.C. Yao, J. Org. Chem. 29 (1964) 2959–2963.
- [37] M.N. Kopylovich, K.T. Mahmudov, A.J.L. Pombeiro, J. Hazard. Mater. 186 (2011), doi:10.1016/j.jhazmat.2010.11.119.
- [38] J. Marten, W. Seichter, E. Weber, Zeitschrift f
 ür anorganische und allgemeine Chemie 631 (2005) 869–877.
- [39] J. Marten, W. Seichter, E. Weber, U. Bohme, J. Phys. Org. Chem. 20 (2007) 716-731.
- [40] C. Bustos, C. Sanchez, R. Martinez, R. Ugarte, E. Schott, C.D. Mac-Leod, M.T. Garland, L. Espinoza, Dyes Pigments 74 (2007) 615–621.
- [41] J. Marten, W. Seichter, E. Weber, U. Bohme, CrystEngComm 10 (2008) 541–547.
- [42] E. Weber, J. Marten, W. Seichter, J. Coord. Chem. 62 (2009) 3401-3410.
- [43] S. Trasatti, Pure Appl. Chem. 58 (1986) 955-966.
- [44] V.V. Pavlishchuk, A.W. Addison, Inorg. Chim. Acta 298 (2000) 97-102.