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Electrochemical studies and semiempirical calculations on π -conjugated dienones and heterocyclic nitrogen containing donor ligand molecules

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Abstract Reduction potentials for the first electron transfer to a broad selection of nitrogen containing bi- and polydentate molecules considered as potential ligands have been determined. Results are compared with data obtained with semiempirical and UV-Vis spectroscopic data. Close correlations for the investigated molecules are observed. Systematic differences in properties of molecules with and without the keto moiety can be explained by invoking molecular orbital and surface interaction arguments. Similar structural arguments can be used to explain the behaviour of 2,4,6-tripyridin-2-yl[1,3,5]triazine. UV-Vis data match closely those derived from HOMO-LUMO calculations for these molecules.

Keywords Heterocycles · Semiempirical calculations · Cyclic voltammetry · Organometal chemistry

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Introduction

N-heterocycles are widely used as ligands in coordination and organometallic chemistry [1] and as building blocks for the generation of supramolecular structures [3, 4, 5, 6, 7, 8]. The degree of complexity of such compounds ranges from simple pyridine to the quincodine systems which have, for example, found broad application in enantioselective *cis*-hydroxylation of olefins [9]. Despite the broad usage of di- and polydentate aromatic heterocycles as connecting units between redox-active transition metal sites [10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22], surprisingly, little is known about the electrochemical behaviour of this class of ligands.

In the present paper, we report the results of a systematic cyclovoltammetric investigation of a broad selection of π -conjugated nitrogen donor molecules and describe the correlation of electrochemical and computational data. The results are supported with a critical review of previously published data. Related data on conjugated quinoxaline derivatives show stepwise (ring by ring) reduction of pyrazine units of the molecules [23]. An increase in the number of connected pyrazines makes reduction more easier because of the conjugation within these molecules.

A selection of 25 N-containing ligands was investigated. Choice and grouping of ligands was based on structural features and similarities. Pyridine-based molecules, where the six-membered heterocycles are either implemented in a condensed system or directly linked to each other or linked via heterocyclic units, are collected in Table 1. Pyridine-based ligands, where the nitrogen heterocycles are spanned by ethylene or more complex π -conjugated bridges, are listed in Table 2. Ligands, where the pyridines or other groups are spanned by 3-oxa-penta-1,4-diene-1,5-diyl or similar fragments, are finally contained in Table 3.

Electrochemical data are initially tentatively interpreted based on structural properties and their

Table 1 Investigated pyridine-based ligands

#	Name and synonyms	Structural formula
1	2,2'-bipyridine	
2	4,4'-bipyridine	
3	[2,2';6,6']terpyridine	
4	2,5-dipyridin-2-yl-pyrazine	
5	2,3-dipyridin-2-yl-pyrazine	
6	1,3,5-tris(2-pyridyl)triazine	
7	[1,10]phenanthroline	
8	2,5-bis(4-pyridinyl)[1,2,4]oxadiazol	

relationship towards electrochemical behaviour as outlined in the examples above. As these correlations tend to be purely empirical and because the structural differences (see e.g. **11**, **12** and **13** or **18** and **19**) are rather minor in some cases, we have employed the semiempirical calculations in addition. The calculated heats of formation of the neutral ligand molecule and the radical anion obtained by electroreduction are compared with the reduction potentials. In addition, energies of the various frontier orbitals are considered. A similar approach has been applied successfully for a large number of nitro-aromatic compounds elsewhere [24], for the reduction of aliphatic compounds [25] and for the oxidation of fluorene derivatives [26]. The use of data derived by a variety of semiempirical methods [27] has been identified as being far superior to traditional approaches in the explanation of structural and substituent effects based on, for example, Hammett constants [28]. It is particularly noteworthy that significant correlations were obtained in most reported cases even without taking into account the solvent effects, i.e. with

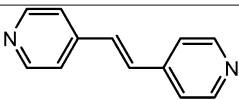
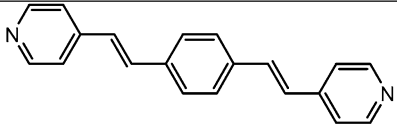
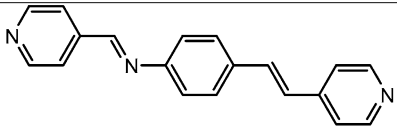
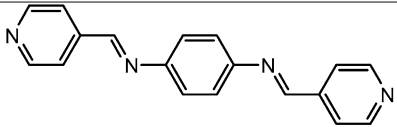
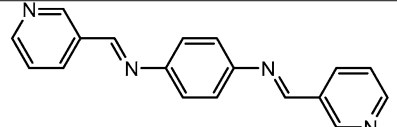
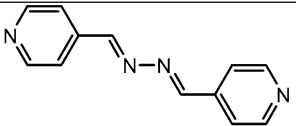
calculated data (heats of reaction, formation etc.) obtained without including solvent shell-molecule interactions. Expansions of available programmes for semiempirical calculations enabling inclusion of at least a generalized solvent shell did not result in significant differences in examples already studied [29].

Experimental

The investigated ligands are collected in Tables 1, 2, 3; they are grouped according to typical structural features and similarities. Compounds **1–3** and **5** were obtained from Aldrich/Sigma-Aldrich, **6** and **9** from Fluka Chemie, **7** from Acros Organics, and were used without further purification. Compound **4** was synthesized according to literature procedures [30], **8** was synthesized and purified according to reference [31], **10–12** [32]; **13** [33]; **14** [34]; **15–18** [35]; **19** [36] **20–25** [35].

Cyclic voltammetry (CV) was performed with a one-compartment glass cell with a platinum disc (1 mm²

Table 2 Investigated benzene-based ligands

#	Name and synonyms	Structural formula
9	1,2-bis(4-pyridinyl)ethylene	
10	1,4-bis(2-(4-pyridinyl)ethenyl)benzene	
11	4-[2-(4-pyridinyl)ethenyl]-N-(4-pyridinylmethylene)-N-benzylamine	
12	N,N'-bis(4-pyridinylmethylene)1,4-benzenediamine	
13	N,N'-bis(3-pyridinylmethylene)1,4-benzenediamine	
14	4-pyridinaldazine	

apparent surface area, 99%, Schiefer, Hamburg) or a glassy carbon disc (HTW, Thierhaupten) embedded into a PTFE¹ cylinder as working electrode. A platinum wire counter electrode and a silver reference electrode (Ag/Ag⁺, 0.01 M AgNO₃ in a solution of 0.1 M tetrabutylammonium hexafluorophosphate TBFP (Fluka, dried in an oil pump vacuum at 120°C) in methylene chloride) were used. For ease of comparison, all electrode potentials are converted using the ferrocene/ferrocinium redox couple as a reference point ($E_{\text{FeC}} = 0$ mV) [37]. In order to compare literature data with our results, additional reference electrodes were constructed based on the information provided by the respective authors. In some cases, incomplete information about the composition of the employed reference electrode might result in some uncertainty. All CVs were run at a scan rate of $dE/dt = 200$ mV s⁻¹ using an electrolyte solution of 0.1 M tetrabutylammonium hexafluorophosphate in methylene chloride with a concentration of the compounds of 5 mM. CVs were recorded using a Voltalab 3.1 potentiostat (Radiometer) equipped with a digital electrochemical analyser DEA 101 and an electrochemical interface IMT 102. All experiments were run at room temperature (25°C) under nitrogen purified with a CuO catalyst for dioxygen removal.

UV-Vis spectroscopy was carried out with a Perkin Elmer Lambda 40 UV-Vis spectrometer using 2 mm

cuvets at a resolution of 1 nm. The concentration of the complexes was 1×10^{-3} M in methylene chloride. The validity of the Lambert-Beer law was confirmed for **17** for concentrations ranging from 10^{-3} M to 10^{-4} M at 25°C.

Semiempirical calculations were carried out on a personal computer using the program GAUSSIAN98W [38] with the method PM3 [39].

Results and discussion

Typical cyclic voltammograms showing the redox behavior of the investigated molecules are shown in Figs. 1–5. In the investigated electrode potential range, mostly one or two reversible one-electron transfer reactions with reduction and oxidation peaks corresponding definitely to each other (although sometimes with considerable splitting of the peak potential) could be identified. By variation of scan rate and cathodic potential limit corresponding redox peaks as used in the subsequent calculation of E_0 were identified and conclusively distinguished from peaks (in particular oxidation peaks) of products formed chemically from the electroreduction products of the investigated ligands. In no case, an influence of the working electrode material (platinum and glassy carbon) could be identified, thus, the following discussion is limited to results obtained with a platinum electrode.

¹PTFE polytetrafluoroethylene

Table 3 Investigated ligands of dienone type

#	Name and synonyms	Structural formula
15	2,5-bis(4-pyridinylmethylene)cyclopentanone	
16	2,5-bis(3-pyridinylmethylene)cyclopentanone	
17	2,5-bis(phenylmethylene)cyclopentanone	
18	2,6-bis(4-pyridinylmethylene)cyclohexanone	
19	2,6-bis(3-pyridinylmethylene)cyclohexanone	
20	2,6-bis(phenylmethylene)cyclohexanone	
21	1-methyl-3,5-bis(4-pyridinylmethylene)piperidin-4-one	
22	1-methyl-3,5-bis(3-pyridinylmethylene)piperidin-4-one	
23	1-isopropyl-3,5-bis(4-pyridinylmethylene)piperidin-4-one	
24	1-isopropyl-3,5-bis(3-pyridinylmethylene)piperidin-4-one	
25	1-benzyl-3,5-bis(4-pyridinylmethylene)piperidin-4-one	

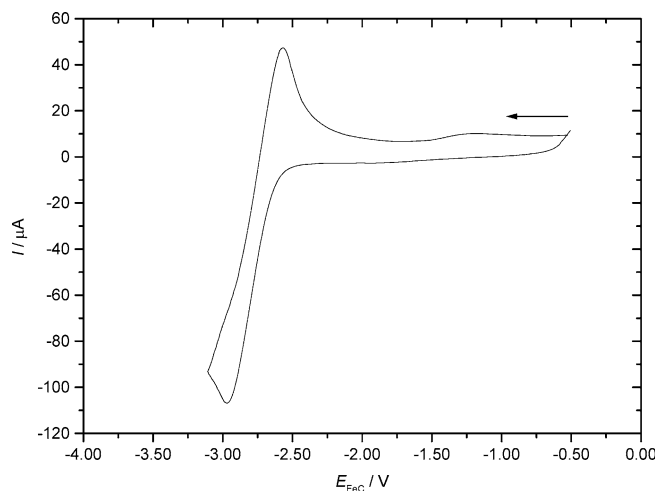


Fig. 1 Cyclic voltammogram of a solution 2,2'-bipyridine (**1**) in THF + 0.1 M $[n\text{-Bu}_4\text{N}][\text{PF}_6]$, 25 °C, under argon, $dE/dt = 200 \text{ mV s}^{-1}$

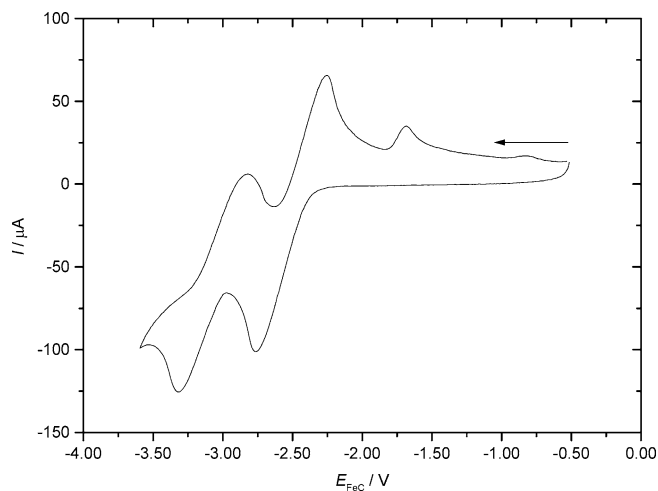


Fig. 2 Cyclic voltammogram of a solution 4,4'-bipyridine (**2**) in THF + 0.1 M $[n\text{-Bu}_4\text{N}][\text{PF}_6]$, 25 °C, under argon, $dE/dt = 200 \text{ mV s}^{-1}$

Pyridine-based ligands

The electroreduction of 2,2'-bipyridine (**1**) has been extensively investigated [40] mostly with polarography and aqueous electrolyte solutions. Based on the height of the polarographic wave a two-electron transfer reaction has been concluded. The CV obtained with a nonaqueous electrolyte solution provides no evidence of a two-electron process (see Fig. 1). The slightly asymmetric shape of the CV is presumably due to the onset of cathodic decomposition of electrolyte solution constituents as observed in a blank CV (not shown here). The redox potential as well as the reduction peak potential (see Table 1) is difficult to compare with the value obtained in an aqueous solution ($E_{1/2} = -1.5 \text{ V}$ vs. calomel electrode filled with aqueous solution 4 M LiCl^2). A study of the reduction of 2,2'-bipyridine in DMF has been reported [41]. Two reduction peaks at $E_{1/2\text{FeC}} = -2.563 \text{ V}$ and -3.198 V were found. The first reduction is shifted to more positive values by about 340 mV when compared with our result, the shift may be caused by solvent effects affecting both the potential of the reference electrode system as well as the reduction potential. Assuming that the second reduction occurs about 640 mV negative to the first reduction it cannot be discerned from the mentioned decomposition reaction in our case. The reduction of free 2,2'-bipyridine in DMF at $T = 54 \text{ °C}$ has been studied [42, 43]. Two reduction peaks at $E_{\text{aq. SCE}} = -2.09 \text{ V}$ and -2.69 V were found. The peak potential difference of 600 mV is very close to the value reported elsewhere [41], comparison of the peak potentials is difficult, because reference is made to an aqueous reference electrode system. Following the suggestion by Strehlow et al. [44] a conversion to the ferrocene scale is feasible, the converted values are

²The value depended slightly on the added alkali hydroxide

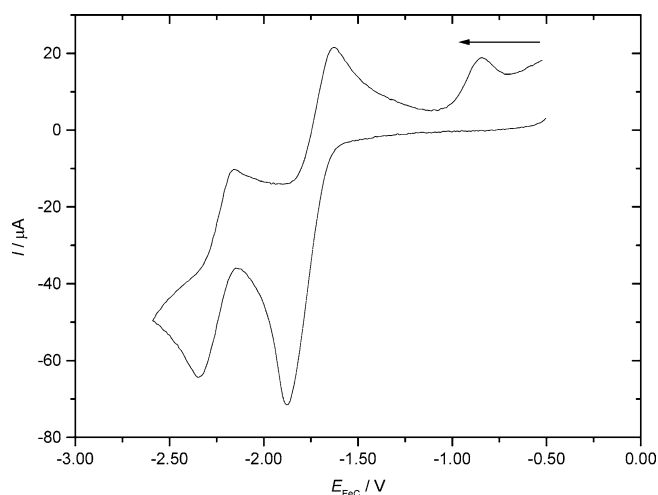


Fig. 3 Cyclic voltammogram of a solution 1,2-di(4-pyridyl)-ethylene (**9**) in THF + 0.1 M $[n\text{-Bu}_4\text{N}][\text{PF}_6]$, 25 °C, under argon, $dE/dt = 200 \text{ mV s}^{-1}$

approx. $E_{\text{ref. FeC}} = -2.25 \text{ V}$ and -2.85 V . The values differ considerably both from those reported by Bra-terman and Song and from those reported here.

Reduction potentials of 2,2'-bipyridine in ruthenium-based complexes have been reported [45], because of the metal-ligand interaction and the different solvent (DMF) the data are incomparable³.

The electroreduction of 4,4'-bipyridine (**2**) in DMF has been studied before [41]. Two reduction processes with $E_{\text{red, FeC}} = -2.394 \text{ V}$ for the first and $E_{\text{red, FeC}} = -2.875 \text{ V}$ for the second (irreversible) process were found. The shift as compared to our data is the same as stated above; the reported difference between the

³In addition, it has been observed in attempts to reproduce the reference electrode potentials, that a concentration of 3 M NaCl in DMF is not at all attainable

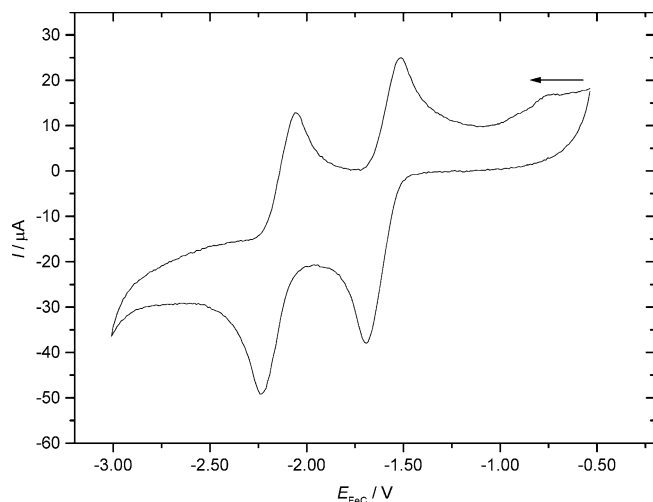


Fig. 4 Cyclic voltammogram of a solution 2,5-bispyridin-4-ylmethylene-cyclopentanone (**15**) in THF + 0.1 M $[n\text{-Bu}_4\text{N}][\text{PF}_6]$, 25 °C, under argon, $dE/dt = 200 \text{ mV s}^{-1}$

reduction potentials is the same as in our case. Comparing both bipyridines **1** and **2** it is evidently easier to reduce 4,4'-bipyridine. This has already been observed by Rusina et al. [46] in a comparative polarographic study. The difference in $E_{1/2}$ amounted to 265 mV and is thus very similar to the data discussed here. The data by Rusina et al. were supported by orbital energy calculations, which showed orbital energies of the participating LUMO (involved in the proceeding electron transfer) in qualitative agreement with the experimental data. Results of our semiempirical calculations are discussed below. In a comparative study of the behaviour of both pyridines at a mercury electrode in contact with acidic and neutral aqueous solutions, a flat adsorption with π -interaction between aromatic system and metal was concluded for the dication (protonated) of 4,4'-bipyri-

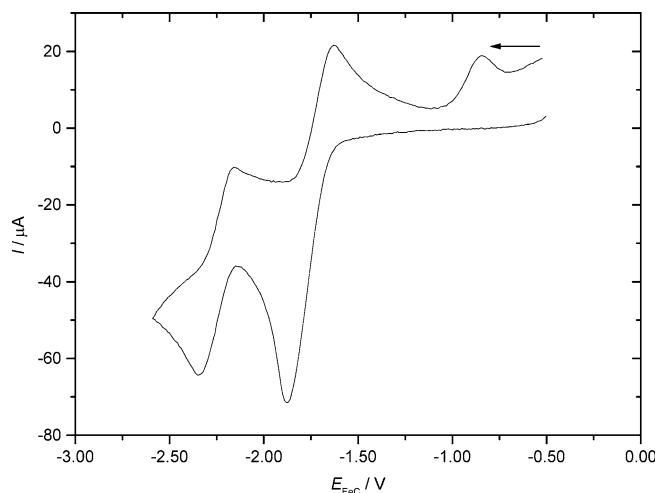


Fig. 5 Cyclic voltammogram of a solution 2,6-di(4-pyridylmethylene)cyclohexanone (**18**) in THF + 0.1 M $[n\text{-Bu}_4\text{N}][\text{PF}_6]$, 25 °C, under argon, $dE/dt = 200 \text{ mV s}^{-1}$

dine. With 2,2'-bipyridine this could be assumed only when the whole molecule was flat after formation of an ethylene bridge between the pyridine units [47]. Neutral forms of **1** and **2** as well as the radical cations are adsorbed in a non-planar arrangement. These conclusions are based entirely on indirect evidence deduced from electrochemical measurements, in the absence of direct evidence gleaned, for example, from *in situ* spectroelectrochemical measurements no direct arguments pertaining to our results reported here can be derived.

Data pertaining to the reduction of **3** ([2,2'; 6,6'] terpyridine) proceeding in a single step only (indicating a lack of electronic communication between the two pyridine units wherein presumably reduction proceeds simultaneously and at the same reduction potential) have not been reported before. The present value of $E_{0,\text{FeC}} = -2.71 \text{ V}$ is slightly positive to the structurally related 2,2'-bipyridine presumably because of enhanced delocalization of the electronic charge in the radical anion.

Reduction potentials of the first and second reduction process of **4** (2,5-dipyridine-2-yl-pyrazine) measured in DMF vs. a reference electrode incompletely specified have been previously reported by Kaim and Kohlmann [48]. Two reduction processes spaced by about 710 mV were reported. Assuming a saturated calomel electrode filled with dimethylformamide saturated with KCl, the first redox potential can be converted to the potential scale employed here. The calculated value of $E_{0,\text{FeC}} = -1.85 \text{ V}$ differs somewhat from our value, taking into account the different solvents and electrolyte salts this is reasonable. In our measurements, two reduction processes spaced almost exactly by the same value of 620 mV were found. Considering the significantly enlarged conjugated aromatic electron system, the positive shift (indicating an easier reduction) as compared to values for **1–3** comes as no surprise. The presence of two reduction waves implies some intramolecular electronic communication causing the reduction of the second pyridine unit to occur at a considerably more negative potential, but this second reduction potential is still well within the range of reduction potentials already observed with bipyridines.

The reduction of **5** (2,3-dipyridine-2-yl-pyrazine) has been observed before. Roffia et al. [42] have studied the reduction in DMF at $T = 54 \text{ °C}$. Three reduction peaks were reported at $E_{\text{aq,SCE}} = -1.93 \text{ V}$; 2.55 V and -2.74 V . Converted to the ferrocene scale (see above) the approximate values are $E_{\text{ref,FeC}} = -2.09 \text{ V}$; -2.71 V and -3.01 V . The first reduction peak corresponding to the single peak observed here is located considerably more positive. Effects of temperature, different solvent, supporting electrolyte are conceivable causes. The second and third peaks reported in both reviewed investigations employing DMF as solvent are presumably not observed here because methylene chloride was used wherein already solvent decomposition occurs at these potentials. Molnar et al. [49] have reduced **5** in acetonitrile. The reported value of $E_{1/2} = -1.91 \text{ V}$ (converted

Table 4 Electrochemical data of compounds **1–25**

Compound	E_0/V	E_{red}/V	E_{oxid}/V	$\Delta E/mV$
1	-2.76	-2.9	-2.56	400
2	-2.51	-2.78	-2.24	540
	-3.08	-3.35	-2.81	540
3	-2.71	-2.90	-2.51	390
4	-2.15	-2.28	-2.01	270
	-2.78	-2.91	-2.64	270
5	-2.51	-2.69	-2.32	370
6	-2.03	-2.19	-1.87	320
	-2.65	-2.79	-2.51	280
	-2.82	-3.00	-2.64	360
7	-2.66	-2.80	-2.51	290
	-2.86	-3.05	-2.76	290
8	-2.17	-2.28	-2.05	230
	-2.52	-2.67	-2.37	300
9	-2.27	-2.42	-2.12	300
	-2.69	-2.82	-2.56	260
10	-2.21	-2.38	-2.03	350
	-2.40	-2.56	-2.23	330
	-2.60	-2.69	-2.51	180
11	-2.06	-2.16	-1.95	210
	-2.35	-2.45	-2.24	210
	-2.73	-2.85	-2.61	240
12	-2.00	-2.16	-1.85	310
	-2.23	-2.39	-2.08	310
	-2.48	-2.61	-2.34	270
13	-2.18	-2.28	-2.09	190
	-2.60	-3.71	-2.48	230
14	-1.92	-2.03	-1.80	230
	-2.30	-2.41	-2.18	230
15	-1.61	-1.70	-1.51	190
	-2.15	-2.25	-2.05	200
16	-1.78	-1.87	-1.69	180
	-2.37	-2.46	-2.28	180
17	-1.92	-2.05	-1.78	270
	-2.56	-2.69	-2.43	260
18	-1.75	-1.88	-1.62	260
	-2.25	-2.34	-2.16	180
19	-1.89	-2.00	-1.79	240
	-2.42	-2.54	-2.29	250
20	-2.07	-2.21	-1.93	280
	-2.60	-2.74	-2.46	280
21	-1.71	-1.81	-1.61	200
	-2.09	-2.18	-1.99	190
22	-1.83	-1.93	-1.73	200
	-2.33	-2.44	-2.23	210
23	-1.85	-1.93	-1.77	160
	-2.29	-2.38	-2.20	180
24	-1.93	-2.04	-1.82	220
	-2.42	-2.51	-2.33	180
25	-1.71	-1.79	-1.62	170
	-2.09	-2.20	-1.99	210

to the ferrocene scale) is similar to the value reported by Roffia et al. [42] and consequently considerably more positive than our value.

Reduction potentials of 1,3,5-tri(2-pyridyl) triazine (**6**) in ruthenium-based complexes have been reported [45], because of the metal-ligand interaction and the different solvent (DMF) the data are difficult to compare. Using Osteryoung square wave voltammetry, the first reduction peak was found at $E_{Ag/AgCl(3M NaCl)} = -0.5$ V. Converted to the ferrocene reference scale employed for clarity in this investigation, this would be

approx. $E_{0,FeC} = -1.31$ V, the value observed here is $E_{0,FeC} = -2.19$ V⁴.

Reduction of **7** ([1,10] phenanthroline) proceeds in two rather closely spaced steps. The value of the first reduction potential is within the range observed with pyridines as discussed above, evidence of an extended conjugated system significantly facilitating reduction is not obvious. Assuming that electrons are subsequently transferred into both nitrogen-containing units the spacing of the two reduction peaks again implies intramolecular electronic communication. Despite the fact that [1,10] phenanthroline has been widely used (e.g. as a complexing agent in analytical chemistry) no electrochemical data have been published.

In **8** (2,5-bis(4-pyridinyl)[1, 2, 4] oxadiazol) the pyridine moieties are linked via a heteroatoms containing unit. Extended conjugation is nevertheless possible. This is manifested in the easier transfer of the first electron. Electronic intramolecular communication is nevertheless evident from the potential difference between the two reduction processes, which evidently result in electrons being transferred separately into the two pyridine subunits. For this compound synthesized recently for the first time no electrochemical data are known.

Benzene-based ligands

In compounds **9–14** pyridine units are linked via ethylene or more complicated bridges. In all cases, at least two reduction waves are observed. It is most likely, that one electron is transferred into every pyridine unit. The spacing of the reduction peaks might be taken as an indicator of the extent of electronic communication with a larger spacing indicating a stronger communication. In all cases, the first reduction proceeds at electrode potentials shifted into positive direction as compared to **1** and **2**. This comes as no surprise because the bridging units provide conjugation between the terminal pyridines thus enlarging the size of the conjugated systems.

There has been only one study of the electroreduction of **9** (1,2-bis(4-pyridinyl)ethylene) in acetonitrile [50]. Two reduction processes at $E_{1/2SCE} = -1.71$ V and -2.02 V were observed. The spacing of about 300 mV is similar to our value of about 400 mV. Conversion into the ferrocene scale assuming that the authors have employed an aqueous reference electrode results in values that are considerably more positive than ours, this again may be caused by the different solvent. In a study of the electroreduction of **9** in aqueous media [51] no data relevant for this work were obtained.

For compounds **10–14** no electrochemical data have been reported previously. When going from **10** to **12** the number of nitrogen atoms in the bridging ethylene units is successively increased from 0 to 2, the first reduction potentials (as well as the subsequent peak potentials) are

⁴Regarding the reproducibility of the reference electrode see the preceding footnote

shifted to less negative values. Beyond the conjugation – which is basically the same in all molecules – facilitating electron transfer the nitrogen atoms being somewhat more electronegative than carbon help in stabilizing the additional negative charge brought by the transferred electron. A minor effect is caused by the position of the nitrogen atom in the terminal pyridine entity. In **12** (*N,N'*-bis(4-pyridinylmethylene)1,4-benzenediamine), the nitrogen atoms are located in the most distant para-position, in **13** (*N,N'*-bis(3-pyridinylmethylene) 1,4-benzenediamine) they are located in the meta-positions. The number of bonds between the terminal nitrogens included in a conceivable conjugated system is reduced from 15 to 13. Accordingly, the reductive electron transfer is somewhat less favourable, the reduction potential for **13** is more negative than for **12**. Compound **14** (4-pyridinaldazine) has a bridging unit different from any other unit discussed so far. Nevertheless, comparison with **9** may be helpful. The considerably lengthened bridge now incorporating two nitrogen atoms obviously increases the size of the conjugated system with the nitrogen atoms helping in stabilizing the negative charge. The shift of the reduction potential to more positive values is consequently significant, it is the most positive of all compounds discussed so far.

Dienone type ligands

In compounds **15–25** the pyridine or benzene terminals are linked via 3-oxa-penta-1,4-diene-1,5-diyl or similar fragments. Most of these compounds have been synthesized most recently, thus, no electrochemical data are available for comparison. In all cases, two reduction peaks are observed. Based on the arguments discussed above, a consecutive electron transfer to the terminals is conceivable; electronic communication between these units causes the occurrence of two peaks instead of one. This obvious argument has a serious drawback. In several compounds, the terminal unit is benzene. Simonet suggested, based on a study of some benzene-terminated molecules, that the radical anion formed during the first electron transfer has a negative charge on the carbonyl oxygen. Unfortunately, nothing is known about the internal charge distribution in the dianion. Comparing the pyridine-free compounds **17** and **20** with their respective pyridine containing counterparts **15/16** and **18/19**, the former show a somewhat more negative reduction potential. Further, as discussed below, this certainly supports the central role of the oxygen-surface interaction, but it also lends some support to the assumption that localization of the negative charge is more favourable on the terminal pyridine units.

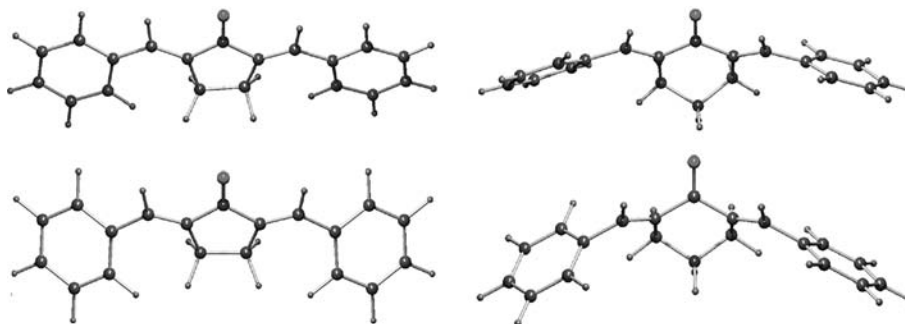
During the electroreduction of **17** (2,5-bis (phenylmethylene) cyclopentanone), two waves at $E_{0\text{FeC}} = -1.92$ V and -2.56 V are found. The spacing agrees with the value observed by Simonet [52], the absolute values are hard to compare as the reference electrode is only incompletely specified and assignment

of the numerous potential values remains ambiguous. During the electroreduction of **20** (2,6-bis (phenylmethylene) cyclohexanone), two waves at $E_{0\text{FeC}} = -2.07$ V and -2.6 V are found. $\Delta E = 530$ mV is similar to the value observed by Simonet [52], the absolute values are hard to compare as the reference electrode is only incompletely specified and assignment of the numerous potential values remains ambiguous. When comparing the second reduction potentials assigned to the reduction of the radical anion formed during the first electroreduction step Simonet observed, that the reduction potentials were almost identical, i.e. the details of the molecular structure (pentanone vs. hexanone ring) did not affect the energetics of this step. In our case, the potentials are also fairly close, whereas the first reduction potentials – as observed by Simonet – are rather different. Reduction of **20** in an aqueous buffer solution was studied by Abd-El-Nabey et al. [53]. Depending on the pH-value, one or two reduction steps were observed. From additional measurements with chemically reduced **20**, it was concluded that the carbonyl group was not involved in the reduction processes studied in this work. This is in striking difference to the assumption of Simonet, wherein reduction proceeds via a negatively charged carbonyl oxygen which subsequently explains the insignificant influence of the molecular structure on the energetics of the second reduction step. Interaction between the carbonyl oxygen and the metal surface has been invoked as an explanation of the rather similar electrochemical behavior of the respective compounds **15** and **16** vs. **17** and **18** and **19** vs. **20**. The absence of pyridyl units in **17** and **20** does not result in large potential differences implying, that pyridine nitrogens are not significantly involved in the ligand-metal interaction leaving the carbonyl-oxygen as the anchoring and interacting site. This difference is most likely caused by the aqueous solutions used by Abd-El-Nabey et al. This is supported by the observation that at low pH-values (about pH = 3.3) only a single wave was found, whereas at higher pH-values two waves could be discerned.

Although some trends and differences could be explained at least quantitatively by looking at the molecular structure and the properties of structural subunits, these explanations remain tentative in most cases they are not quantitative at all. Thus, we have employed semiempirical calculations to find similar trends in calculated data, which are based in turn on molecular structures, internal charge distributions etc. If such correlations exist the assumed calculation conditions might help in understanding the electrochemical data.

For the computational calculations, we used the semiempirical method PM3, since it offers a rapid access to thermodynamic and electronic data of large molecules. *Ab initio* quantum chemical methods (e.g. MP2 or higher) in combination with large basis sets would most likely provide more accurate results, but would also require much longer times for computation.

Fig. 6 Comparison of the solid-state structures of 2,5-dibenzylidene cyclopentanone **17** (top, left) and 2,6-dibenzylidene cyclohexanone **20** (top, right) with the respective calculated structures (bottom)



Solvent and surface effects play an important role in electrochemical processes proceeding in a condensed phase at a phase boundary. They cannot be calculated with sufficient accuracy with any computational method. Therefore, semiempirical as well as *ab initio* methods assuming the molecules under study to be in the gas phase are not expected to support the results of cyclic voltammetry in every detail, but nevertheless, a correlation of computational and electrochemical data should be possible.

Molecular geometries of organic compounds obtained by PM3 are generally in good agreement with the results of solid-state structures: for example, the solid-state structures of 2,5-dibenzylidene cyclopentanone (**17**) [54, 55, 56] and 2,6-dibenzylidene cyclohexanone (**20**) [57] are compared with the results of the PM3 calculations in Fig. 6. From computational investigations, heats of reaction (H_R ; $L + e^- \rightarrow L^-$), the energy of the LUMO and the HOMO (molecules L) and the energy of the SOMO (molecules L^-) have been obtained (see Table 2).

The negative heats of reaction indicate exothermicity of the electron transfer in the gas phase. More negative heats of reaction should correlate with less negative

electrochemically determined E_0 values (easier reduction). However, the correlation of these data clearly shows a pronounced difference between the conjugated dienones **15–25** on one hand and compounds **1–14** on the other (see Fig. 7).

With respect to the calculated heats of reaction, the dienones **15–25** show reduction potentials which are about 0.4–0.6 V more positive than those of **1–14**. Obviously, the dienones **15–25** are easier to reduce than compounds **1–14**, although they show similar heats of reaction in the gas phase. Since it is not probable that this feature is due to systematic errors in the computational method we used, it should be related to specific differences in the electrochemistry or interfacial chemistry of these two classes of compounds.

Correlation of the calculated LUMO energies (the orbital, where the electron is transferred to) of compounds **1–25** with the electrochemically determined E_0 values provides a similar picture (Fig. 8).

Although the LUMO energies of the dienones **15–25** are in the same range as those of **1–14**, the two groups can clearly be distinguished by correlating these data with the experimental E_0 values. However, for generation of the trendlines in Fig. 8, one member (compound

Fig. 7 Correlation of the calculated heats of reaction of **1–25** with the electrochemically determined E_0 values (♦ and —: compounds **1–8**; ■ and —: compounds **9–14**; ▲ and —: compounds **15–25**)

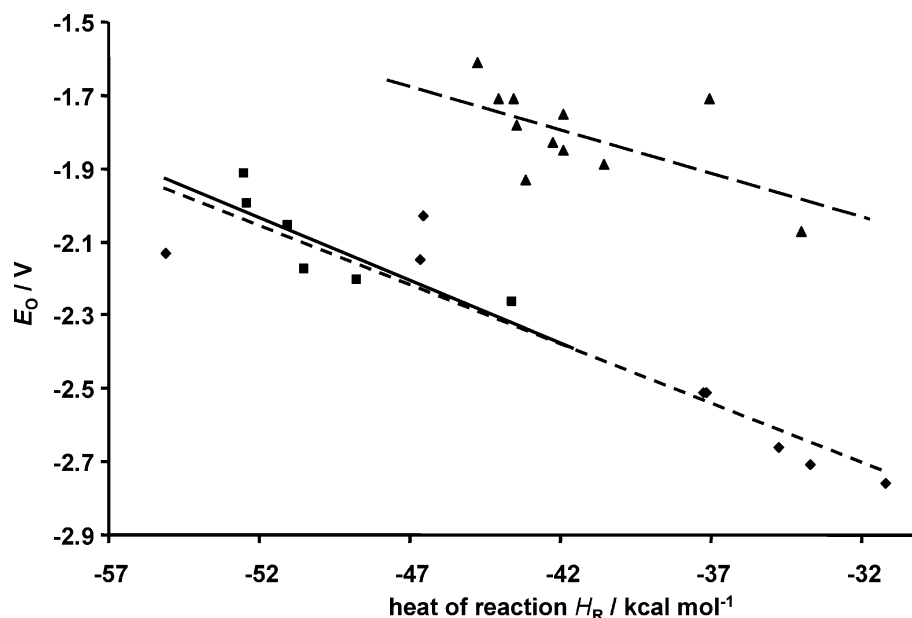
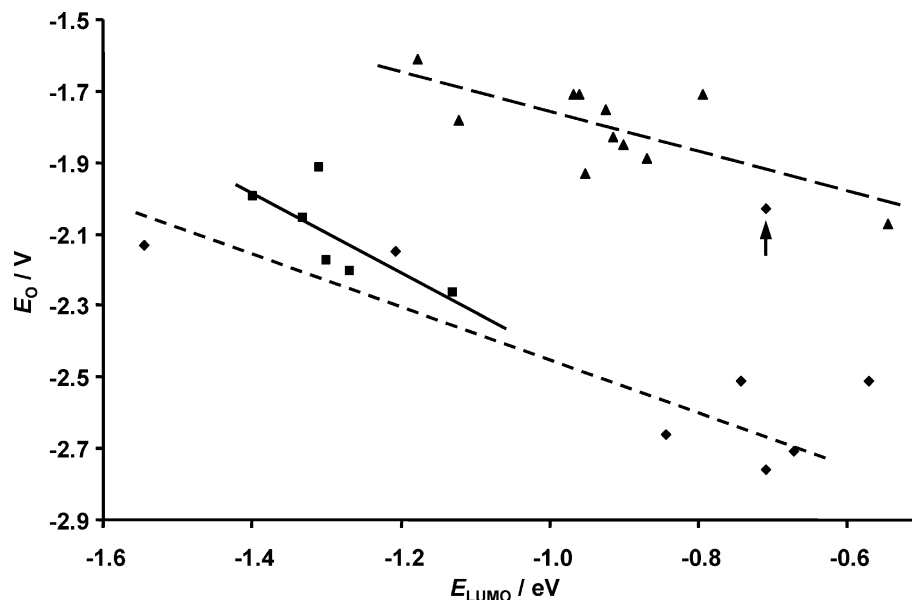


Fig. 8 Correlation of the calculated LUMO energies of compounds 1–25 with the electrochemically determined E_0 values (◆ and —: compounds 1–8; ■ and —: compounds 9–14; ▲ and —: compounds 15–25)



6, for chemical structure see Fig. 1) of group 1 was neglected. It is marked with an arrow in Fig. 8 and will be discussed in more detail below. This compound almost behaves like one of the dienones 15–25: its reduction potential is shifted with respect to its LUMO energy by about 0.6 V to a more positive potential, making it much easier to reduce than the other compounds of group 1.

Correlation of the SOMO (Semi Occupied Molecular Orbital) energies of the radical anions L^- of 1–25 with the electrochemical data (Fig. 9) again shows an analogous behaviour as in the correlations above: the dienones 15–25 can clearly be distinguished from compounds 1–14.

However, compound 6, which was excluded from the calculation of the trendline for the group 1 ligands in

Fig. 8, now fits nicely into the correlation. This suggests a closer look at the molecular structure of this ligand (see below).

There are two plausible ways for molecules 1–25 to interact with the surface of an electrode:

- coordination via the lone electron pairs of the sp^2 -hybridized nitrogen atoms
- coordination via the π -conjugated skeleton (including the carbonyl group in compounds 15–25).

In the present environment, the platinum (and according to our observations even the glassy carbon) electrode can be regarded as an arrangement of atoms in a low-oxidation state. From a series of structurally characterized compounds, it is known that

Fig. 9 Correlation of the calculated SOMO energies of compounds 1–25 with the electrochemically determined E_0 values (◆ and —: compounds 1–8; ■ and —: compounds 9–14; ▲ and —: compounds 15–25)

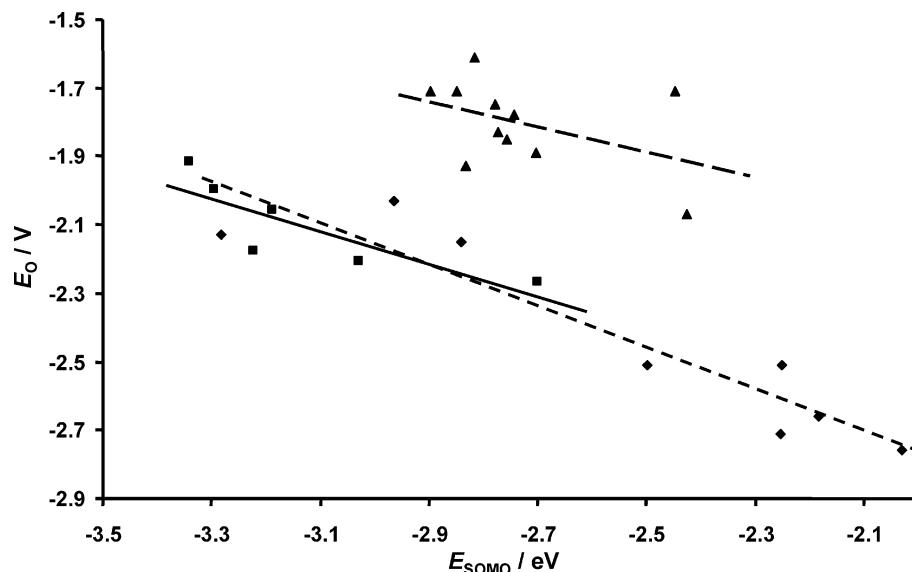


Table 5 Computational data of compounds **1–25**

Compound	H_F of L (kcal/mol)	H_F of L^- (kcal/mol)	$\Delta H_R: L + e^- \rightarrow L^-$ (kcal/mol)	E_{HOMO} of L (eV)	E_{LUMO} of L (eV)	$E_{HOMO}-E_{LUMO}$ (eV)	E_{SOMO} of L^- (eV)	E_0/V
1	62.475	31.290	-31.185	-9.329	-0.710	8.620	-2.029	-2.76
2	62.061	24.806	-37.255	-10.062	-0.743	9.320	-2.251	-2.51
3	94.652	60.930	-33.723	-9.260	-0.672	8.587	-2.254	-2.71
4	102.875	56.211	-46.664	-9.265	-1.207	8.058	-2.841	-2.15
5	105.707	68.566	-37.141	-9.828	-0.572	9.256	-2.498	-2.51
6	146.556	100.003	-46.553	-10.110	-0.709	9.401	-2.963	-2.03
7	71.386	36.659	-34.726	-9.149	-0.843	8.306	-2.183	-2.66
8	83.956	28.869	-55.087	-9.818	-1.545	8.273	-3.283	-2.13
9	75.143	31.581	-43.562	-9.350	-1.128	8.221	-2.697	-2.27
10	112.421	63.726	-48.695	-8.735	-1.265	7.469	-3.025	-2.21
11	120.845	69.836	-51.009	-8.910	-1.329	7.581	-3.185	-2.06
12	129.248	76.885	-52.363	-9.137	-1.396	7.741	-3.293	-2.00
13	128.467	78.029	-50.438	-8.955	-1.299	7.657	-3.220	-2.18
14	118.222	65.764	-52.458	-9.670	-1.307	8.363	-3.338	-1.92
15	50.275	5.511	-44.764	-9.779	-1.178	8.602	-2.816	-1.61
16	49.822	6.371	-43.451	-9.534	-1.122	8.412	-2.743	-1.78
17	35.708	-1.325	-37.033	-9.217	-0.793	8.424	-2.447	-1.71
18	48.703	6.813	-41.891	-9.850	-0.925	8.926	-2.779	-1.75
19	48.320	7.778	-40.541	-9.583	-0.870	8.713	-2.702	-1.89
20	34.317	0.312	-34.005	-9.271	-0.546	8.726	-2.425	-2.07
21	60.905	17.360	-43.544	-9.484	-0.967	8.517	-2.849	-1.71
22	60.589	18.344	-42.244	-9.404	-0.915	8.489	-2.773	-1.83
23	50.978	7.810	-43.168	-9.447	-0.952	8.495	-2.833	-1.93
24	50.708	8.798	-41.910	-9.376	-0.901	8.475	-2.758	-1.85
25	89.205	45.148	-44.057	-9.471	-0.960	8.510	-2.896	-1.71

α,β -unsaturated ketones are coordinating to low-valent late transition metals via their π -orbitals [58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71]. A prominent example is $Pd_2(dba)_3$ (dba = dibenzylidene acetone), wherein each Pd atom is coordinated by one C=C double bond of each dba molecule [72, 73, 74]. However, there are structurally characterised complexes of α,β -unsaturated ketones known, where the C=O double bond is also involved in binding of the metal. This is mainly the case, when the metal centres are becoming more Lewis acidic [75, 76, 77, 78, 79, 80] e.g. in the iron complexes (Ph-CH=CH-C(=O)-CH₃)Fe(CO)₂(PR₃) [75]. An excellent model for a surface bound 3-oxa-penta-1,4-diene is the cluster Os₃(CO)₉(L) (L = 4-phenylcyclohexa-2,5-dienone), where the ligand is bound to three osmium atoms with both C=C double bonds and the C=O double bond [81]. All these findings are corroborated by results of quantum chemical calculations by different groups on the adsorption of enones on platinum surfaces [82, 83, 84].

Table 6 Selected spectroscopic and calculated data for **15–20**

Compound	$E_{HOMO}-E_{LUMO}$ (eV)	$\lambda_{max,calc}/nm$	λ_{max}/nm
15	8.602	144.1	332
16	8.412	147.4	342
17	8.424	147.2	350
18	8.926	138.8	306
19	8.713	142.3	321
20	8.726	142.1	327

From the Dewar-Chatt-Duncanson model [85, 86], we know that both the HOMO (π -donor) as well as the LUMO (π -acceptor) play a role in the description of the binding of olefins to (late) transition metals. Applying this model to explain the interaction between an α,β -unsaturated ketone and the atoms of an electrode surface implies a close interaction between the surface and the electron accepting orbital, which should give rise to a low barrier for the electron transfer (Fig. 10, left). This binding mode is supported by the fact that compounds **17** and **20**, which are dienones without a pyridyl ring, show a rather similar electrochemical behaviour as the pyridine-containing members of the dienone group.

In contrast, pyridines are known to interact with low-valent late transition metal centres by σ donation of the lone-pair of the nitrogen donor sites. For the adsorption of pyridine and related ligands, like cinchonidine and quinidine, on metal surfaces the situation is slightly different: pyridine adsorbs on a platinum surface in a tilted mode, coordinating to the surface with its lone-pair of electrons at the nitrogen atom [87, 88]. The mode of adsorption of larger molecules like quinchonidine and quinidine depends on the molecular structure of the adsorbent, on its concentration, and the surface coverage and can therefore be mediated by the lone-pair or by the π system [89, 90, 91]. These results can be extended to the binding of pyridines to the platinum atoms of an electrode surface (Fig. 10, right), which presumably involves the lone-pair of electrons at the nitrogen atom. However, the LUMO of a hetero aromatic base like pyridine has π -character, which prevents a direct communication between the drain (LUMO) and the source

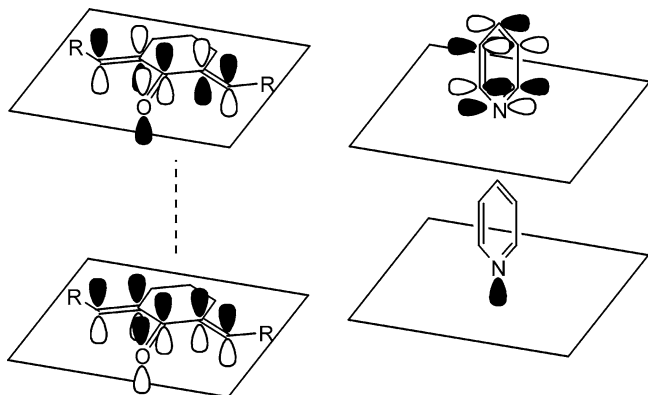


Fig. 10 Interaction of characteristic frontier orbitals of dienones and pyridines with the surface of a platinum electrode

(Pt surface) of the electron transfer. This is also consistent with a study of Thiel et al., who investigated the electrochemical behaviour of the ferrocenyl site and the $\text{Mo}(\text{CO})_4$ fragment in 5-ferrocenyl-3-(2-pyridyl)pyrazole $\text{Mo}(\text{CO})_4$ complexes [92]. No electronic communication between the two redox-active sites could be found since the π -conjugation is interrupted at the linkage between the N,N' -chelating ligand and the $\text{Mo}(\text{CO})_4$ moiety.

In electrochemistry, an additional overpotential will be needed to transfer an electron to a pyridine type of molecule compared to an enone (described above). The frontier orbitals of all dienones are of π -character, the lone-pair at the pyridyl rings belongs to the σ -skeleton, while the electron has to be transferred to a π -type orbital. This is in our opinion the reason for the different electrochemical behaviour of these two classes of compounds.

The different behaviour of compound **6** in the correlation of the electrochemical data with the calculated LUMO energies (Fig. 8) can be explained by its special steric and electronic situation. On one hand, the 1,3,5-tripyrityl-triazine possesses the most extended π -system of all class 1 molecules and on the other hand, the triazine ring is electron deficient due to three nitrogen atoms in the ring. These features may favour an interaction between the π -system and the electrode surface over a σ attack.

Support for the applicability of the semiempirical calculations and even for the limited influence of solvent effects can be gleaned from a correlation of observed electronic transition bands in UV-Vis spectra and the transition energies calculated as described above. Figure 11 shows the results for a representative selection. The generally lower wavelengths (i.e. higher transition energies) observed with the cyclopentanone linking unit might be related to a structure-specific minor solvent-molecule interaction effect. A further comparison of results obtained with various semiempirical methods has been reported elsewhere [27]. An increased precision with more demanding basis sets resulted indeed in only

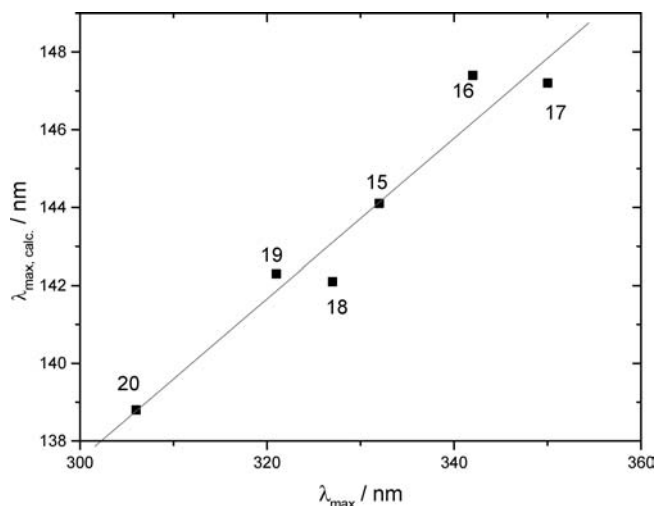


Fig. 11 Correlation of experimentally observed UV-Vis absorption maxima with transition energies obtained from semiempirical calculations

incrementally better correlations in a study of the electroreduction of chalcones.

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