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Electrogeneration of (*Z*)-α-aroyloxy-β-aroylthiostilbenes and (*Z*)-4,5-diaryl-2-arylimino-1,3-oxathioles by cathodic reduction of monothiobenzils in the presence of electrophilic reagents. Computational B3LYP and RI-MP2 study on the relative stability of oxathiole compounds

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ABSTRACT

Electrochemical reductions of monothiobenzils in the presence of either aroyl or carbonimidoyl dichlorides were carried out, yielding products with sulfur retention. Electrolyses in the presence of aroyl chlorides led to previously unknown (*Z*)-α-aroyloxy-β-aroylthiostilbenes in high to quantitative yields, whereas reactions in the presence of arylcarbonimidoyl dichlorides provided novel 4,5-diaryl-2-arylimino-1,3-oxathioles in fair to high yields. The molecular structures of (*Z*)-α-benzoyloxy-β-benzoylthio-4,4′-dimethylstilbene and (*Z*)-2-(2,4-dichlorophenylimino)-4,5-diphenyl-1,3-oxathiole were determined by X-ray crystallography. Also, ab initio HF, density functional B3LYP, and Møller–Plesset RI-MP2 procedures were applied to oxathiole compounds revealing that (*Z*)-isomers are more stable than (*E*)-isomers and that both isomers are separated by a relatively low activation barrier.

1. Introduction

Electrochemical reductions of benzils in protic media lead to benzoins through two-electron, two-proton processes.[1–3] However, electrolyses in aprotic media carried out in the presence of non-electroactive electrophilic reagents have a demonstrably higher synthetic interest, since under these conditions the electrogenerated intermediates can attack these reagents instead of undergoing simple protonation.[4–7] On this basis we developed effective preparative processes for enediol diesters by cathodic reduction in the presence of acylating agents.[8–10]

With a view to expanding this synthetic methodology, we have established that carbonimidoyl dichlorides,[11] which are inexpensive and easily available reagents,[12,13] show optimal chemical and electrochemical properties to be exploited. They were found to be reducible at relatively high cathodic potentials, providing isocyanides in near quantitative yields,[14,15] but also showed ability to act exclusively as geminal dielectrophilic agents, thereby capturing reactive intermediates generated by electroreduction of benzils,[16,17] furils,[18] or anils[19] at lower cathodic potentials, yielding 2-arylimino-4,5-diaryl-1,3-dioxoles, 2-arylimino-4,5-di(2-furyl)-1,3-dioxoles or 3,4,5-triaryl-2-aryliminooxazolines, respectively.

Monothiobenzils[20–27] are also easily available compounds that can be prepared from chlorodeoxybenzoins by reaction with sodium thiosulfate followed by the treatment with sodium hydroxide. These substances, like thiones,[28] exhibit a remarkable proclivity to undergo desulfuration in polar reactions, yielding either benzils or products that would be expected when starting from benzils; e.g., in ethanolic solution, monothiobenzil is slowly converted to benzil with evolution of hydrogen sulfide, whereas the treatment of monothiobenzil with hydroxylamine leads to benzil dioxime.[26] Conversely, cycloaddition reactions, in general, occur with retention of sulfur, leading to thioheterocyclic compounds. Consequently, synthetic research has mainly focused on this particular reactivity.[20,21,24,25,27] However, mild electrochemical methodology, seemingly optimal to attempt preparative processes with sulfur retention, remained unexplored.

Given the good results obtained with the work on electroreduction of benzils in the presence of acyl and carbonimidoyl chlorides, we persevered in expanding our research project,

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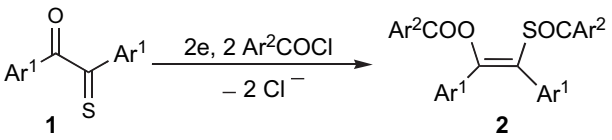
studying possible applications of this methodology to monothiobenzils. A preliminary communication on cathodic acylations leading to monothiostilbenediol derivatives was reported.[29] In this paper, we report full details of that work along with the results of a number of electroreductive reactions of monothiobenzil in the presence of carbonimidoyl dichlorides that have been demonstrated to provide an excellent approach to (*Z*)-2-arylimino-4,5-diphenyl-1,3-oxathioles. Spectroscopic properties and X-ray crystallographic molecular structures of novel compounds are also reported. Finally, a computational B3LYP and RI-MP2 study on the relative stability of isomeric oxathiole compounds was also carried out in order to explain the observed stereoselectivity.

The chemistry of oxathioles has been extensively reviewed.[30–32] Regarding 2-imino-1,3-oxathioles, the standard synthetic procedure involves the reaction of phenacyl bromides with either a dithiocarbamate or a thiourea.[33] Compounds of this type can also be synthesized by decomposition of an α-diazoketone in the presence of an isothiocyanate.[33] Further specific reactions yielding 2-imino-1,3-oxathioles have been reported.[34–43]

2. Results and discussion

Monothiobenzils **1** and aroyl chlorides (ratio 1:2) were added and dissolved in the catholyte. After a short time these solutions changed to an intensive blue colour because of the change of polymerized monothiobenzils to the monomeric state.[22,23] Then, electrolyses were carried out at constant cathodic potentials under which the role of aroyl chlorides, being non-electroactive, is limited to that of electrophilic agents, which react with the nucleophilic intermediates electrogenerated from monothiobenzils. The electricity consumption was 2 F in all cases. Single electrolysis products were formed and isolated and, after applying the usual instrumental techniques, were identified as (*Z*)-α-benzoyloxy-β-benzoylthiostilbenes **2** (Scheme 1). Yields ranged from fair to quantitative. Geometrical characteristics of this new class of compounds were determined by single crystal X-ray crystallography of **2g**, showing that the C=C double bond adopts a (*Z*) configuration. The molecular structure found is illustrated in Fig. 1. The steric interactions force the *p*-tolyl rings out of the plane (interplanar angle of the two *p*-tolyl rings=116.5°, torsion angles: C46–C41–C3–C2=29.7° and C16–C11–C2–C3=67.1°). Table 1 shows a comparison between X-ray selected bond lengths and bond angles and those computed at three different levels of theory, the ab initio HF/6-31G(d), and two density functional procedures, the well known B3LYP/6-31G(d), and the newer, but computationally more demanding, wB97X-D/6-31G (d). This Table shows an excellent agreement between experimental



entry	Ar^1	Ar^2	Yield (%)
a	C_6H_5	C_6H_5	89
b	C_6H_5	4-ClC_6H_4	91
c	C_6H_5	4-$CH_3C_6H_4$	78
d	4-$CH_3OC_6H_4$	C_6H_5	80
e	4-$CH_3OC_6H_4$	4-ClC_6H_4	60
f	4-$CH_3OC_6H_4$	4-$CH_3C_6H_4$	84
g	4-$CH_3C_6H_4$	C_6H_5	88
h	4-$CH_3C_6H_4$	4-ClC_6H_4	94
i	4-$CH_3C_6H_4$	4-$CH_3C_6H_4$	95
j	4-ClC_6H_4	C_6H_5	89
k	4-ClC_6H_4	4-ClC_6H_4	70
l	4-ClC_6H_4	4-$CH_3C_6H_4$	76

Scheme 1.

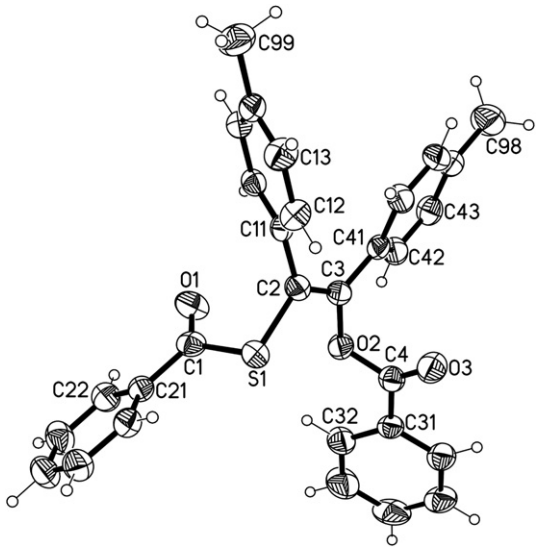


Fig. 1. Thermal ellipsoid plot (50% level) of compound **2g** in the crystal.

Table 1
Selected bond lengths and bond angles of crystal and calculated structures in crystal structure of **2g**

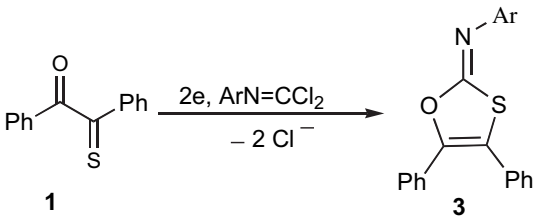
Bond	Crystal structure (Å)	Calculated structure (Å)[a]	Calculated structure (Å)[b]	Calculated structure (Å)[c]
S1–C2	1.783 (2)	1.789	1.792	1.780
C2–C3	1.339 (3)	1.325	1.352	1.344
O2–C3	1.408 (3)	1.383	1.400	1.388
O2–C4	1.369 (3)	1.337	1.370	1.361
C2–C11	1.484 (3)	1.493	1.484	1.482
S1–C1	1.795 (2)	1.795	1.831	1.814
Bond angle	**Crystal structure (°)**	**Calculated structure (°)[a]**	**Calculated structure (°)[b]**	**Calculated structure (°)[c]**
C3–C2–S1	119.50 (17)	119.93	120.38	120.48
C4–O2–C3	116.43 (17)	120.25	118.98	119.14
C2–C3–O2	117.7 (17)	119.98	119.26	119.40
C2–S1–C1	98.77 (11)	101.46	101.55	101.67
C3–C2–C11	124.0 (2)	123.55	123.97	123.33
C2–C3–C41	128.1 (2)	126.09	126.88	126.48

Geometries optimized at the following levels of theory.
[a] HF/6-31G(d).
[b] B3LYP/6-31G(d).
[c] wB97X-D/6-31G(d).

X-ray crystallography data and the calculated molecular structures of **2g**, which confirms the accuracy of the computational methodology applied to envisage molecular geometries (the small differences might be ascribed to molecular distortion in the crystal structure induced by packing effects).

As in the case of electroreductions of diaryl-1,2-diketones, these reactions showed stereoselectivity toward the formation of *Z* isomers. This seems to be attributable to chelation of electrogenerated intermediates with electrolyte metal cations.[44] This is the first electrochemical synthetic process developed from monothiobenzils. Considering the pronounced proclivity of monothiobenzils to undergo desulfuration reactions, these findings are notable.

In view of the good results obtained by studying electroreductive acylations of monothiobenzils, our objective was to explore the possibility of formation of 2-arylimino-4,5-diphenyl-1,3-oxathioles by electrochemical reduction of monothiobenzil in the presence of arylcarbonimidoyl dichlorides (Scheme 2).



1 **3**

entry	Ar	Yield (%)
a	C_6H_5	53
b	4-ClC_6H_4	74
c	2,4-$Cl_2C_6H_3$	71
d	2,6-$Cl_2C_6H_3$	63
e	4-BrC_6H_4	75
f	4-NCC_6H_4	56

Scheme 2.

Electrolyses were carried out following an experimental procedure similar to that applied in electroreductive acylation reactions but using the geminal dielectrophilic agents in ratio 1:1. These processes also consumed 2 F, leading to products that were identified as the targeted compounds. Yields ranged from moderate to high. The stereochemical arrangements of products **3a** and **3c** were established by X-ray crystallographic analysis showing that the C=N double bond adopt a (*Z*) configuration. The molecular structure found for **3c** is illustrated in Fig. 2. The oxathiole ring is planar (mean deviation 0.009 Å) and the dimensions of the ring agree well with average values of four other 2-imino-1,3-oxathioles (refcodes: BEQCEG, HEJCEE, JUTJAJ, VEYRUM) found in the Cambridge Database;[45] maximum deviations are 0.01 Å and 1.3°. The substituent rings C11–16, C21–26 and C31–36 subtend interplanar angles of 78.0, 35.7, and 39.1° with the central ring, all rotated in the same sense. The packing (Fig. 3) involves layers of molecules parallel to the *yz* plane at $x \approx 1/4, {}^{3}/_{4}$; molecules are linked by the weak hydrogen bonds C24–H24···N (H···N 2.66 Å, angle 172°) and C34–H34···S (H···S 2.97 Å, angle 127°). Table 2 shows a comparison between X-ray selected bond lengths and bond angles of **3c** and those computed at three different levels of theory, the ab initio HF/6-31G(d), the density functional B3LYP/6-31G(d), and the modified Møller–Plesset RI-MP2/6-31G(d). As previously found for **2g**, there

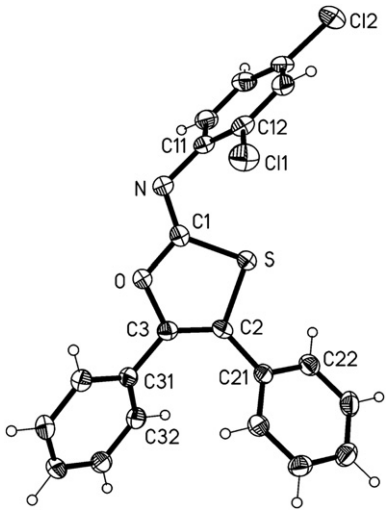


Fig. 2. Thermal ellipsoid plot (50% level) of compound **3c** in the crystal.

is a good agreement between experimental X-ray crystallography data and the calculated molecular structures of **3c** (the RI-MP2 procedure is significantly more elaborate than the others but, as we show below, the use of this high level method is necessary to explain why the (*Z*)-isomers are the exclusive species).

The exclusive isolation of products **3** with (*Z*) stereochemistry can be explained on the basis of our conclusions from previous work on electrosynthesis and topomerization of aryliminodioxoles.[18,46] These compounds exhibit a remarkably low configurational stability around the carbon–nitrogen double bond causing topomerization processes that were studied by HF and B3LYP computational methodology, showing relatively small E_a and $\Delta G^{\neq}_{298}$ values, close to 12 and 13 kcal/mol, respectively. With this purpose, and in order to gain further insights into the isomerization process of compounds **3**, the transition state (TS) optimized structures for the thermal (*Z*)–(*E*) interconversion of products **3a** and **3f** were determined at the B3LYP/6-31G(d) level of theory and characterized by vibrational frequency calculations that gave a sole imaginary frequency for the TS structure. The computed TSs for **3a** and **3f** are shown in Fig. 4. The CNC angles are 176.4° and 162.3°, respectively, and this reveals that there is a small deviation from the inversion mechanism in favor of the rotational one,[46] especially for **3f**. Also, it is interesting to note that the aryl group changes its configuration to almost orthogonal with the five-membered ring in the transition state (82.9° for **3a** and 88.2° for **3c**), which can be attributed to a gain of stabilization by orbital overlapping and also by lessening of steric hindrance. In addition, there is a shortening of the bond C=N in the TS with respect to the ground state (1.262 Å→1.221 Å for **3a** and 1.266 Å→1.232 Å for **3c**). This fact supports the view that a rotation process taking place through a polar mechanism is not involved in the isomerization process since under these conditions these bonds might be expected to lengthen. Finally, the activation energies (E_a) including ZPE and thermal corrections for **3a** and **3f** were obtained at the same level as geometry optimizations as the difference between the total molecular energy of the transition state TS and that of the ground state. The values found were small, just 12.41 and 11.38 kcal/mol, whereas the values of $\Delta G^{\neq}_{298}$ were 12.09 and 11.57 kcal/mol. It should be noted that these kinds of processes are so fast that the resulting isomers cannot be separated at room temperature.[47] The values of E_a for rotational barriers around a C=N bond range between very low (<10 kcal/mol) and extremely high (>70 kcal/mol) values.[46] We have found values of ≈12 kcal/mol, which reveals the easy isomerization around the C=N bond.

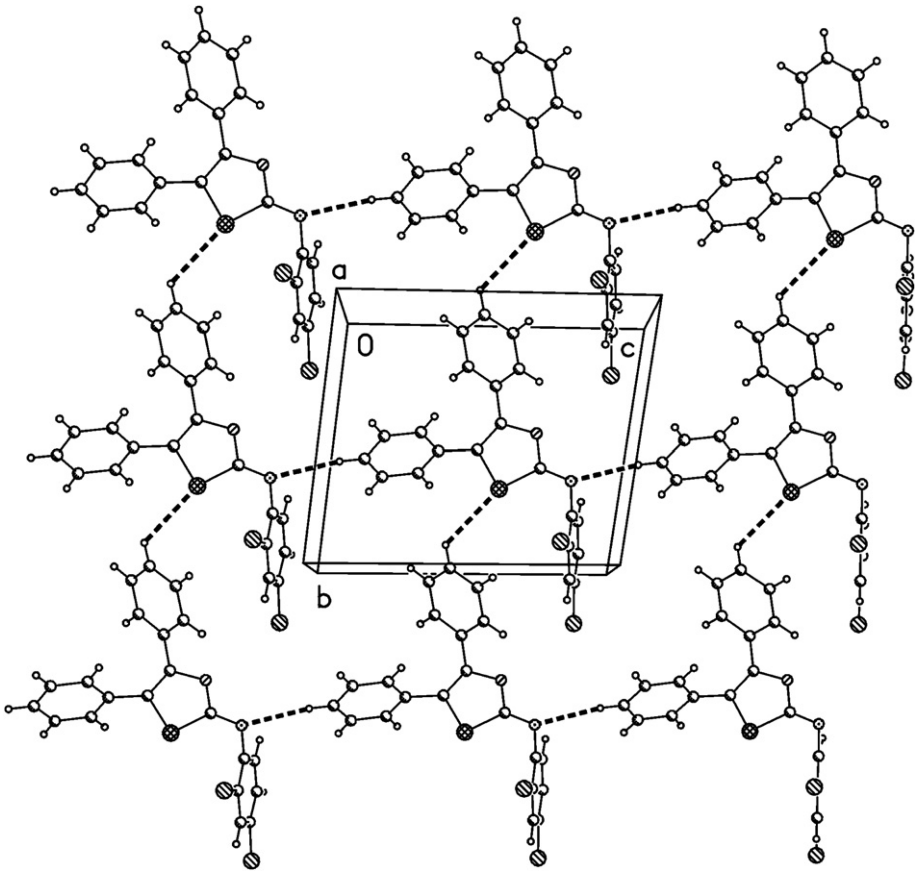


Fig. 3. Packing diagram of compound **3c** showing weak hydrogen bonds (dashed lines).

Table 2
Selected bond lengths and bond angles of crystal and calculated structures in crystal structure of **3c**

Bond	Crystal structure (Å)	Calculated structure (Å)[a]	Calculated structure (Å)[b]	Calculated structure (Å)[c]
S–C1	1.754 (2)	1.769	1.794	1.772
S–C2	1.763 (2)	1.776	1.783	1.762
C1–O	1.361 (2)	1.338	1.361	1.367
O–C3	1.398 (2)	1.371	1.388	1.389
C2–C3	1.339 (3)	1.326	1.353	1.358
Bond angle	**Crystal structure (°)**	**Calculated structure (°)[a]**	**Calculated structure (°)[b]**	**Calculated structure (°)[c]**
C1–S–C2	90.29 (10)	89.67	89.89	89.90
S–C2–C3	110.7 (2)	110.23	110.49	110.88
C2–C3–O	115.0 (2)	115.07	114.89	114.93
C3–O–C1	112.9 (2)	115.07	114.74	113.05
O–C1–S	111.17 (14)	109.94	109.92	111.22

Geometries optimized at the following levels of theory.
[a] HF/6-31G(d).
[b] B3LYP/6-31G(d).
[c] RI-MP2/6-31G(d).

Relative stabilities and population distribution of **3**-(*Z*),(*E*) stereoisomeric pairs have been computed at two different levels of theory, B3LYP/6-31G(d) and RI-MP2/6-31G(d), and the results are shown in Table 3. These results make it clear that (*Z*)-isomers show a higher stability than (*E*)-isomers, such that in all cases (*Z*)-isomers are the predominant population at both levels of theory. However, values of the *Z*/*E* ratio computed at the B3LYP level show some scatter and for this reason a higher level procedure, the RI-MP2 method, was also used. The *Z*/*E*-values obtained with this procedure demonstrate that (*Z*)-isomers are always in a ratio $\geq$80%, which, in turn, gives rise to its exclusive crystallization by a continuous shift of the equilibrium toward the *Z*-form as crystallization progresses.

In order to get experimental evidence to confirm that the formation of electrolysis products involves radical anion nucleophilic intermediates electrogenerated from monothiobenzils and the subsequent chemical reaction with the added electrophiles, some electroanalytical experiments were carried out. Thus, the reduction of **1a** is a quasireversible **1e** process when cyclic voltammetry is performed by switching the direction of the scan at −0.85 V (under these conditions a second **1e** wave that appears at more negative potential (−1.1 V) is prevented). As has been reported,[48] this second wave is due to the formation of a dianion, which avoids the appearance of the wave of the first process. The peak potential, E_p, for the first process corresponds to −0.72 V at 1 V/s. In turn, the electrophile shows a single wave with E_p=−1.81 V (Ph–N=CCl_2).

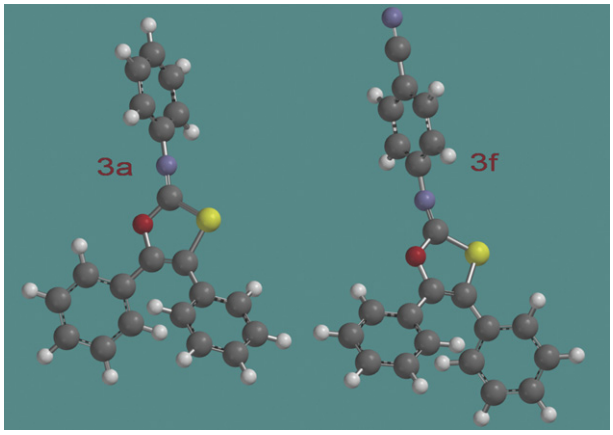


Fig. 4. Optimized TS structures for **3a** and **3f** computed at the B3LYP/6-31G(d) level of theory.

Table 3
Relative stabilities and *Z*/*E* ratio-values of the isomers of compounds **3** computed at the B3LYP/6-31G(d) and RI-MP2/6-31G(d) levels of theory

Compound	B3LYP/6-31G(d)			RI-MP2/6-31G(d)		
	ΔE	ΔG^0_{298}	*Z*/*E*	ΔE	ΔG^0_{298}	*Z*/*E*
3a	−0.41	−0.30	62:38	−1.31	−1.45	92:8
3b	+0.02	−0.46	69:31	−0.90	ND	82:18
3c	−0.88	−2.10	97:3	−0.79	ND	79:21
3d	−0.52	−0.15	56:44	−0.79	ND	79:21
3e	−0.03	−0.69	76:24	−0.88	ND	82:18
3f	−0.03	−0.18	58:42	−0.76	−0.97	84:16

ΔE=difference between the total molecular energy of the isomers *Z* and *E* (kcal/mol) ΔG^0_{298}=difference between the free energy of the isomers *Z* and *E* at 298 K (kcal/mol). ND: not determined. The population of both isomers in the equilibrium was computed at 298 K by applying the Boltzmann distribution $\frac{N_Z}{N_E} = e^{-\Delta G^0/RT}$, and expressed as values of the *Z*/*E* ratio (in those cases where the ΔG^0 values were not available, the corresponding values of ΔE were used).

Addition of Ph−N=CCl_2 to solutions of monothiobenzil results in the disappearance with time of the wave corresponding to the electrophilic reagent, while the first wave remains due to the formation at the same potential of an active reaction intermediate (A-ECl•) see Scheme 3. Cyclic voltammograms obtained at different scan rates without and in the presence of electrophilic agents support the idea that process takes place through an ECEC mechanism. On the other hand, (PhCOCl) exhibits a peak potential at −1.42 V, showing that the only electroactive compound is monothiobenzil under the preparative electrolysis conditions. It should be noted that in a related work on cathodic acylation of 1,2-diketones we found clear evidence for the electrogeneration of radical anion intermediates.[10]

Summarizing, it can be stated that over the years, the preparation of 2-arylimino-1,3-oxathioles has been encouraged by a versatile reactivity, providing them with a notable usefulness as synthetic intermediates.[32,34,36,49–53] In view of the anticancer[54–56] and some other biological activities recently detected in certain members of the family,[57–59] the progress on the synthesis of aryliminooxathioles is a subject of renewed interest. In this context, it is noteworthy that novel and effective methods for the stereoselective synthesis of the previously unattainable families of compounds **2** and **3** are reported. These are the first examples of electroorganic synthesis from monothiobenzils. Given the retention of sulfur, these reactions provide evidence of a great potential for expanding the chemistry of this class of compounds.

3. Experimental

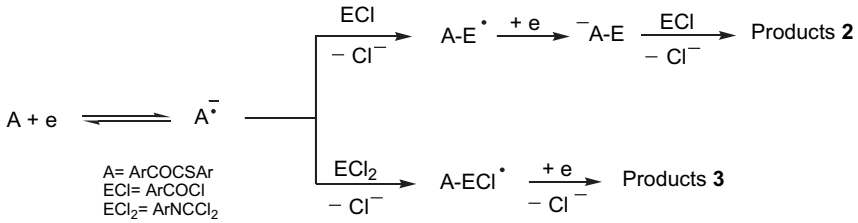
3.1. General

NMR spectra were determined on Bruker AV-200, Bruker AV-300 or Bruker AV-400 with tetramethylsilane as internal reference. Electron-impact mass spectra were obtained on Thermoquest trace MS spectrometer under an ionizing voltage of 70 eV. IR spectra (Nujol emulsions) were recorded on a Nicolet Impact 400 Spectrometer. Microanalyses were performed on a Carlo Erba EA-1108 analyzer. Melting points were determined on a Büchi Melting point B-540 and are uncorrected. Preparative electrochemical experiments were performed with an Amel 552 potentiostat coupled to an Amel 721 integrator. Voltammetric measurements were performed at 298 K with a potentiostat/galvanostat AUTOLAB-100 (Eco-Chemie, Utrecht) using a one compartment three electrode system with a hanging mercury drop electrode. A Ag/AgCl/KCl (saturated) electrode was the reference and a platinum plate was the auxiliary electrode. Monothiobenzils **1** were prepared starting from the corresponding benzoins, which were halogenated, treated with sodium thiosulfate, and finally with sodium hydroxide according to the protocol described by Bak and Praefcke.[20,21] Carbonimidoyl dichlorides **2** were prepared by standard procedures.[12,60]

All computations were performed with the Spartan'08 package program.[61] The most stable conformers were determined by using the MMFF molecular mechanics method. Next, these conformers were used as input for ab initio molecular orbital, density functional theory, and Møller–Plesset calculations of geometry optimizations at the Hartree–Fock, B3LYP, wB97X-D, and RI-MP2 levels of theory with the 6-31G(d) basis set. Frequency calculations were performed at the same level of theory as the geometry optimizations to characterize the stationary points as local minima (equilibrium structures) and to evaluate the zero-point energy (ZPE). No scaling procedures were used.

3.2. Electrogeneration of products 2 and 3

The electrochemical generation of products **2** was performed in a cylindrical cell[62] following the experimental procedure previously reported.[29,63] Products **3** were generated by a similar procedure but using dimethylformamide instead of acetone. Monothiobenzils **1** (5 mmol) were reduced under nitrogen atmosphere, in the presence of either aroyl chlorides (10 mmol) or



Scheme 3.

carbonimidoyl dichlorides (5 mmol) at cathodic potentials ranging between −0.70 and −1.0 V versus SCE. These potentials were selected in order to provide operative current intensities. The average current densities were close to 15 mA/cm^2 at the beginning and 0.9 mA/cm^2 at the end. The cell voltage values remained below 5 V in all cases. The electricity consumption was 2 F for all cases. All electrolysis products were isolated by dropping the catholyte solution into cold brine (200 mL) and filtering or extracting the mixture with diethyl ether. The isolated products were crystallized from the appropriate solvent.

*3.2.1. (Z)-α-Benzoyloxy-β-benzoylthiostilbene (**2a**).* Yield 89%; crystallization from methanol gave white needles mp 123–124 °C. (Found: C, 76.96; H, 4.68; S, 7.31. $C_{28}H_{20}O_3S$ requires: C, 77.04; H, 4.62; S, 7.35); ^{1}H NMR δ ($CDCl_3$, 300 MHz): 7.12–7.25 (m, 6H), 7.30–7.60 (m, 10H), 7.88 (d, 2H, *J*=7.2 Hz), 8.12 (d, 2H, *J*=7.2 Hz); ^{13}C NMR δ ($CDCl_3$, 75.4 MHz): 119.98, 127.54, 127.82, 128.03, 128.12, 128.53, 128.58, 128.94, 129.05, 129.09, 130.21, 130.29, 133.51, 133.65, 134.41, 136.49, 137.77, 152.74, 164.27, 188.43; MS, *m*/*z* (%): 436 (M^+, 29), 300 (50), 315 (43), 299 (72), 121 (46), 106 (61), 105 (100), 77 (84); IR (Nujol): 1732, 1673, 1450, 1248, 1206, 1085, 1066, 902, 695 cm^{-1}.

*3.2.2. (Z)-α-(4-Chlorobenzoyloxy)-β-(4-chlorobenzoylthio)stilbene (**2b**).* Yield 91%; crystallization from methanol gave white needles mp 139–140 °C. (Found: C, 66.66; H, 4.03; S, 6.31. $C_{28}H_{18}Cl_2O_3S$ requires: C, 66.54; H, 3.59; S, 6.34); ^{1}H NMR δ ($CDCl_3$, 300 MHz): 7.10–7.50 (m, 14H), 7.81 (d, 2H, *J*=8.7 Hz), 8.04 (d, 2H, *J*=8.7 Hz); ^{13}C NMR δ ($CDCl_3$, 75.4 MHz): 119.84, 127.44, 128.11, 128.24, 128.29, 128.97, 129.07, 129.16, 129.34, 130.37, 131.67, 134.25, 134.86, 137.57, 140.18, 140.46, 152.91, 163.50, 187.26; MS, *m*/*z* (%): 504 (M^+, 3), 349 (12), 33 (46), 140 (72), 139 (100), 121 (29), 111 (54), 77 (31); IR (Nujol): 1737, 1679, 1464, 1378, 1256, 1210, 1172, 1084, 1015, 902 cm^{-1}.

*3.2.3. (Z)-α-(4-Methylbenzoyloxy)-β-(4-methylbenzoylthio)stilbene (**2c**).* Yield 78%; crystallization from methanol gave white prisms mp 129–130 °C. (Found: C, 77.50; H, 5.24; S, 6.96. $C_{30}H_{24}O_3S$ requires: C, 77.56; H, 5.21; S, 6.90); ^{1}H NMR δ ($CDCl_3$, 200 MHz): 2.33 (s, 3H), 2.37 (s, 3H), 7.11–7.24 (m, 10H), 7.29–7.34 (m, 2H), 7.41–7.47 (m, 2H), 7.78 (d, 2H, *J*=8.2 Hz), 8.01 (d, 2H, *J*=8.3 Hz); ^{13}C NMR δ ($CDCl_3$, 50.3 MHz): 21.71, 21.77, 120.17, 126.40, 127.73, 127.81, 128.08, 128.15, 129.02, 129.20, 129.32, 130.39, 130.42, 134.18, 134.71, 138.10, 144.46, 144.55, 152.81, 164.42, 188.15; MS, *m*/*z* (%): 464 (M^+, 9), 329 (10), 313 (56), 120 (18), 119 (100), 105 (13), 91 (99), 77 (16), 65 (30); IR (Nujol): 1732, 1669, 1604, 1461, 1248, 1209, 1176, 1090, 903 cm^{-1}.

*3.2.4. (Z)-α-Benzoyloxy-β-benzoylthio-4,4′-dimethoxystilbene (**2d**).* Yield 80%; crystallization from methanol gave white needles mp 150–153 °C. (Found: C, 72.51; H, 4.90; S, 6.50. $C_{30}H_{24}O_5S$ requires: C, 72.56; H, 4.87; S, 6.46); ^{1}H NMR δ ($CDCl_3$, 300 MHz): 3.74 (s, 3H), 3.76 (s, 3H), 6.49 (d, 2H, *J*=9.0 Hz), 6.57 (d, 2H, *J*=9.0 Hz), 7.21–7.42 (m, 10H), 7.81 (d, 2H, *J*=8.6 Hz), 8.04 (d, 2H, *J*=8.6 Hz); ^{13}C NMR δ ($CDCl_3$, 75.4 MHz): 55.20, 113.72, 113.83, 127.71, 128.93, 129.03, 130.10, 130.54, 131.58, 131.64, 135.03, 140.05, 140.35, 152.05, 159.25, 160.10, 163.62, 188.94; MS, *m*/*z* (%): 497 (M^++1, 9), 496 (M^+, 22), 375 (9), 359 (20), 151 (16), 135 (20), 105 (100), 77 (33); IR (Nujol): 1738, 1658, 1605, 1510, 1462, 1254, 1173, 1088, 1034, 904, 835, 707 cm^{-1}.

*3.2.5. (Z)-α-(4-Chlorobenzoyloxy)-β-(4-chlorobenzoylthio)-4,4′-dimethoxystilbene (**2e**).* Yield 60%; crystallization from hexane gave yellow prisms mp 139–141 °C. (Found: C, 63.65; H, 3.90; S, 5.72. $C_{30}H_{22}Cl_2O_5S$ requires: C, 63.72; H, 3.92; S, 5.67); ^{1}H NMR δ ($CDCl_3$, 300 MHz): 3.53 (s, 3H), 3.56 (s, 3H), 6.50 (d, 2H, *J*=8.9 Hz), 6.57 (d, 2H, *J*=9.0 Hz), 7.04 (d, 2H, *J*=9.0 Hz), 7.13–7.21 (m, 6H), 7.61 (d, 2H, *J*=8.7 Hz), 7.84 (d, 2H, *J*=8.7 Hz); ^{13}C NMR δ ($CDCl_3$, 75.4 MHz): 55.11, 113.68, 113.77, 126.65, 127.55, 128.89, 129.01, 130.05, 130.50, 131.55, 131.61, 134.95, 140.00, 140.31, 152.00, 159.20, 160.06, 163.60, 187.64; MS, *m*/*z* (%): 566 (M^++2, 8), 564 (M^+, 11), 409 (23), 393 (30), 286 (9), 155 (11), 151 (31), 139 (100), 135 (46), 113 (36), 111 (48), 77 (22); IR (Nujol): 1743, 1680, 1603, 1504, 1462, 1253, 1171, 1080, 1012, 898, 831 cm^{-1}.

*3.2.6. (Z)-α-(4-Methylbenzoyloxy)-β-(4-methylbenzoylthio)-4,4′-dimethoxystilbene (**2f**).* Yield 84%; crystallization from ether/hexane gave white prisms mp 149–152 °C. (Found: C, 73.37; H, 5.30; S, 6.16. $C_{32}H_{28}O_5S$ requires: C, 73.26; H, 5.38; S, 6.11); ^{1}H NMR δ ($CDCl_3$, 300 MHz): 2.35 (s, 3H), 2.38 (s, 3H), 3.73 (s, 3H), 3.76 (s, 3H), 6.68 (d, 2H, *J*=8.7 Hz), 6.76 (d, 2H, *J*=8.7 Hz), 7.14–7.27 (m, 6H), 7.37 (d, 2H, *J*=8.7 Hz), 7.77 (d, 2H, *J*=8.1 Hz), 8.00 (d, 2H, *J*=8.1 Hz); ^{13}C NMR δ ($CDCl_3$, 75.4 MHz): 21.69, 21.75, 55.21, 113.62, 113.73, 118.20, 126.61, 127.25, 127.72, 129.30, 130.38, 130.58, 130.69, 131.61, 134.38, 144.33, 144.49, 144.51, 151.99, 159.08, 159.91, 164.58, 188.59; MS, *m*/*z* (%): 524 (M^+, 21), 389 (31), 373 (39), 286 (9), 151 (34), 135 (43), 119 (100), 91 (83), 65 (35); IR (Nujol): 1736, 1603, 1510, 1463, 1251, 1173, 1081, 897, 828, 746 cm^{-1}.

*3.2.7. (Z)-α-Benzoyloxy-β-benzoylthio-4,4′-dimethylstilbene (**2g**).* Yield 88%; crystallization from methanol gave white plates mp 159–161 °C. (Found: C, 77.58; H, 5.15; S, 6.84. $C_{30}H_{24}O_3S$ requires: C, 77.56; H, 5.21; S, 6.90); ^{1}H NMR δ ($CDCl_3$, 300 MHz): 2.25 (s, 3H), 2.28 (s, 3H), 6.96–7.04 (m, 4H), 7.22 (d, 2H, *J*=8.1 Hz), 7.33–7.43 (m, 6H), 7.46–7.57 (m, 2H), 7.87 (d, 2H, *J*=7.8 Hz), 8.11 (d, 2H, *J*=7.8 Hz); ^{13}C NMR δ ($CDCl_3$, 75.4 MHz): 21.35, 21.42, 119.27, 127.64, 128.58, 128.64, 128.90, 128.97, 129.04, 129.28, 130.23, 130.31, 131.80, 133.47, 133.62, 135.15, 136.82, 137.64, 139.11, 152.58, 164.42, 188.71; MS, *m*/*z* (%): 465 (M^++1, 24), 464 (M^+, 52), 343 (53), 327 (71), 135 (60), 119 (62), 106 (74), 91 (61), 77 (100), 65 (20), 51 (43); IR (Nujol): 1738, 1658, 1605, 1510, 1462, 1254, 1173, 1088, 1034, 904, 835 cm^{-1}.

*3.2.8. (Z)-α-(4-Chlorobenzoyloxy)-β-(4-chlorobenzoylthio)-4,4′-dimethylstilbene (**2h**).* Yield 94%; crystallization from methanol gave white prisms mp 154–156 °C. (Found: C, 67.63; H, 4.10; S, 5.94. $C_{30}H_{22}Cl_2O_3S$ requires: C, 67.54; H, 4.16; S, 6.01); ^{1}H NMR δ ($CDCl_3$, 300 MHz): 2.26 (s, 3H), 2.29 (s, 3H), 6.96–7.05 (m, 4H), 7.20 (d, 2H, *J*=8.1 Hz), 7.30–7.41 (m, 6H), 7.81 (d, 2H, *J*=8.7 Hz), 8.03 (d, 2H, *J*=8.7 Hz); ^{13}C NMR δ ($CDCl_3$, 75.4 MHz): 21.27, 21.34, 118.92, 127.54, 128.89, 128.93, 130.08, 131.40, 131.54, 134.72, 134.93, 137.77, 139.27, 139.94, 140.24, 152.52, 163.43, 187.34; MS, *m*/*z* (%): 534 (M^++2, 30), 532 (M^+, 39), 377 (55), 361 (76), 141 (100), 119 (72), 111 (88), 91 (64), 75 (48); IR (Nujol): 1736, 1675, 1595, 1463, 1259, 1202, 1172, 1091, 906 cm^{-1}.

*3.2.9. (Z)-α-(4-Methylbenzoyloxy)-β-(4-methylbenzoylthio)-4,4′-dimethylstilbene (**2i**).* Yield 95%; crystallization from methanol gave white prisms mp 169–171 °C. (Found: C, 77.93; H, 5.75; S, 6.45. $C_{32}H_{28}O_3S$ requires: C, 78.02; H, 5.73; S, 6.51); ^{1}H NMR δ ($CDCl_3$, 300 MHz): 2.24 (s, 3H), 2.27 (s, 3H), 2.33 (s, 3H), 2.36 (s, 3H), 6.94–7.03 (m, 4H), 7.13–7.23 (m, 6H), 7.34 (d, 2H, *J*=8.1 Hz), 7.77 (d, 2H, *J*=8.1 Hz), 8.00 (d, 2H, *J*=8.4 Hz); ^{13}C NMR δ ($CDCl_3$, 75.4 MHz): 21.34, 21.39, 21.67, 21.74, 119.33, 126.57, 127.71, 128.84, 128.92, 129.03, 129.27, 130.23, 130.36, 131.94, 134.33, 135.33, 137.49, 138.97, 144.31, 144.41, 152.50, 164.48, 188.36; MS, *m*/*z* (%): 492 (M^+, 8), 357 (11), 341 (47), 135 (11), 119 (100), 91 (67), 65 (14); IR (Nujol): 1732, 1672, 1605, 1462, 1455, 1377, 1262, 1176, 1095, 901 cm^{-1}.

*3.2.10. (Z)-α-Benzoyloxy-β-benzoylthio-4,4′-dichlorostilbene (**2j**).* Yield 89%; crystallization from methanol gave white powder mp 136–138 °C. (Found: C, 66.50; H, 4.06; S, 6.28. $C_{28}H_{18}Cl_2O_3S$

requires: C, 66.54; H, 3.59; S, 6.34); ^{1}H NMR δ ($CDCl_3$, 200 MHz): 7.15–7.61 (m, 14H), 7.87 (d, 2H, J=7.3 Hz), 8.10 (d, 2H, J=7.3 Hz); ^{13}C NMR δ ($CDCl_3$, 50.3 MHz): 127.68, 128.68, 128.71, 128.79, 130.35, 130.50, 131.68, 132.86, 133.83, 133.96, 134.11, 135.38, 136.20, 136.44, 152.16, 164.27, 188.21; MS, m/z (%): 506 (M^++2, 14), 504 (M^+, 19), 385 (31), 383 (36), 369 (41), 367 (47), 157 (38), 155 (50), 139 (49), 105 (100), 77 (87); IR (Nujol): 1737, 1678, 1489, 1462, 1246, 1210, 1085, 902, 687 cm^{-1}.

*3.2.11. (Z)-α-(4-Chlorobenzoyloxy)-β-(4-chlorobenzoylthio)-4,4′-dichlorostilbene (**2k**).* Yield 70%; crystallization from methanol gave white powder mp 146–148 °C. (Found: C, 58.64; H, 2.80; S, 5.65. $C_{28}H_{16}Cl_4O_3S$ requires: C, 58.56; H, 2.81; S, 5.58); ^{1}H NMR δ ($CDCl_3$, 200 MHz): 7.16–7.26 (m, 6H), 7.29–7.46 (m, 6H), 7.81 (d, 2H, J=8.6 Hz), 8.03 (d, 2H, J=8.6 Hz); ^{13}C NMR δ ($CDCl_3$, 50.3 MHz): 127.06, 128.75, 128.78, 128.97, 129.18, 130.41, 131.62, 131.66, 132.50, 134.29, 134.57, 135.57, 135.80, 140.73, 152.13, 163.38, 186.96; MS, m/z (%): 572 (M^+, 6), 419 (15), 405 (24), 401 (38), 246 (11), 155 (36), 139 (100), 111 (54), 75 (36); IR (Nujol): 1744, 1681, 1585, 1486, 1463, 1255, 1206, 1087, 1012, 903 cm^{-1}.

*3.2.12. (Z)-α-(4-Methylbenzoyloxy)-β-(4-methylbenzoylthio)-4,4′-dichlorostilbene (**2l**).* Yield 76%; crystallization from methanol gave white needles mp 112–114 °C. (Found: C, 67.49; H, 4.20; S, 5.96. $C_{30}H_{22}Cl_2O_3S$ requires: C, 67.54; H, 4.16; S, 6.01); ^{1}H NMR δ ($CDCl_3$, 300 MHz): 2.32 (s, 3H), 2.37 (s, 3H), 7.14–7.26 (m, 10H), 7.36 (d, 2H, J=8.4 Hz), 7.76 (d, 2H, J=8.1 Hz), 7.98 (d, 2H, J=8.1 Hz); ^{13}C NMR δ ($CDCl_3$, 75.4 MHz): 21.75, 21.81, 120.03, 126.00, 127.75, 128.62, 128.65, 129.42, 130.40, 130.46, 131.68, 132.97, 133.88, 133.96, 135.24, 136.34, 144.83, 144.90, 152.02, 164.35, 187.91; MS, m/z (%): 534 (M^++2, 0.4), 532 (M^+, 1), 397 (1), 383 (5), 381 (7), 120 (24), 119 (100), 91 (40); IR (Nujol): 1739, 1673, 1606, 1487, 1463, 1257, 1206, 1174, 1083, 1012, 897 cm^{-1}.

*3.2.13. (Z)-2-(Phenylimino)-4,5-diphenyl-1,3-oxathiole (**3a**).* Yield 53%; crystallization from acetonitrile gave white needles mp 137–138 °C. (Found: C, 76.70; H, 4.63; N, 4.19; S, 9.79. $C_{21}H_{15}NOS$ requires: C, 76.57; H, 4.59; N, 4.25; S, 9.73); ^{1}H NMR δ ($CDCl_3$, 200 MHz): 7.09–7.49 (m, 15H); ^{13}C NMR δ ($CDCl_3$, 75.4 MHz): 113.53, 121.06, 124.68, 127.58, 128.27, 128.48, 128.99, 129.10, 129.28, 129.66, 130.07, 142.01, 148.59, 161.07; MS, m/z (%): 329 (M^+, 71), 330 (17), 226 (24), 165 (36), 121 (98), 105 (92), 77 (100); IR (Nujol): 1659, 1621, 1591, 1487, 1447, 1246, 1164, 1121, 1070, 960, 831, 764, 691, 646 cm^{-1}.

*3.2.14. (Z)-2-(4-Chlorophenylimino)-4,5-diphenyl-1,3-oxathiole (**3b**).* Yield 74%; crystallization from methanol gave white needles mp 116–117 °C. (Found: C, 69.58; H, 3.92; N, 3.80; S, 8.79. $C_{21}H_{14}ClNOS$ requires: C, 69.32; H, 3.88; N, 3.85; S, 8.81); ^{1}H NMR δ ($CDCl_3$, 200 MHz): 7.04 (d, 2H, J=8.7 Hz), 7.24–7.34 (m, 10H), 7.46 (dd, 2H, J=1.5, 7.5 Hz); ^{13}C NMR δ ($CDCl_3$, 50.4 MHz): 113.46, 122.40, 127.49, 128.04, 128.43, 129.00, 129.02, 129.07, 129.07, 129.30, 129.65, 129.77, 142.09, 146.99, 161.46; MS, m/z (%): 365 (M^++2, 0.6), 363 (M^+, 2), 226 (3), 165 (7), 137 (2), 121 (100), 105 (72), 77 (55); IR (Nujol): 1658, 1651, 1615, 1587, 1484, 1456, 1377, 1217, 1175, 1130, 1086, 1069, 962, 846, 831, 761, 720, 706, 691 cm^{-1}.

*3.2.15. (Z)-2-(2,4-Dichlorophenylimino)-4,5-diphenyl-1,3-oxathiole (**3c**).* Yield 71%; crystallization from methanol gave white needles mp 128–129 °C. (Found: C, 63.42; H, 3.25; N, 3.49; S, 8.02. $C_{21}H_{13}Cl_2NOS$ requires: C, 63.32; H, 3.29; N, 3.52; S, 8.05); ^{1}H NMR δ ($CDCl_3$, 200 MHz): 7.06 (d, 1H, J=8.5 Hz), 7.21 (d, 1H, J=2.2 Hz), 7.25–7.36 (m, 8H), 7.45 (d, 3H, J=2.1 Hz); ^{13}C NMR δ ($CDCl_3$, 50.4 MHz): 114.01, 122.52, 127.63, 127.72, 127.99, 128.18, 128.54, 129.09, 129.19, 129.21, 129.49, 129.60, 130.10, 130.19, 142.53, 144.54, 163.28; MS, m/z (%): 399 (M^++2, 0.7), 397 (M^+, 1), 362 (M^+−Cl, 0.3), 226 (3), 203 (1), 165 (8), 121 (100), 105 (86), 77 (67); IR (Nujol): 1656, 1650, 1620, 1494, 1449, 1311, 1262, 1219, 1185, 1133, 1088, 1071, 1053, 1030, 873, 847, 828, 782, 767, 752, 706, 690, 592 cm^{-1}.

*3.2.16. (Z)-2-(2,6-Dichlorophenylimino)-4,5-diphenyl-1,3-oxathiole (**3d**).* Yield 63%; crystallization from acetonitrile gave white needles mp 207–210 °C. (Found: C, 63.12; H, 3.32; N, 3.50; S, 7.94. $C_{21}H_{13}Cl_2NOS$ requires: C, 63.32; H, 3.29; N, 3.52; S, 8.05); ^{1}H NMR δ ($CDCl_3$, 200 MHz): 7.00 (t, 1H, J=7.78 Hz), 7.24–7.37 (m, 10H), 7.46 (s, 2H); ^{13}C NMR δ ($CDCl_3$, 50.4 MHz): 164.17, 143.01, 142.43, 129.48, 129.38, 129.09, 129.04, 129.02, 128.60, 128.42, 127.96, 127.58, 127.46, 125.13, 114.52; MS, m/z (%): 399 (M^++2, 0.4), 397 (M^+, 0.6), 226 (3), 203 (1), 151 (1), 138 (1), 109 (2), 105 (77), 89 (4), 77 (57), 73 (2), 50 (4); IR (Nujol): 1666, 1634, 1441, 1436, 1224, 1130, 1084, 1065, 1030, 962, 790, 761, 714, 696, 674, 650 cm^{-1}.

*3.2.17. (Z)-2-(4-Bromophenylimino)-4,5-diphenyl-1,3-oxathiole (**3e**).* Yield 75%; crystallization from acetonitrile gave colorless plates mp 122–123 °C. (Found: C, 61.90; H, 3.48; N, 3.39; S, 7.89. $C_{21}H_{14}BrNOS$ requires: C, 61.77; H, 3.46; N, 3.43; S, 7.85); ^{1}H NMR δ ($CDCl_3$, 300 MHz): 6.99 (d, 2H, J=8.4 Hz), 7.26–7.31 (m, 9H), 7.45–7.48 (m, 3H); ^{13}C NMR δ ($CDCl_3$, 75.4 MHz): 113.42, 117.45, 122.78, 127.44, 127.96, 128.39, 128.94, 128.99, 129.03, 129.27, 129.69, 132.56, 142.04, 147.42, 161.33; MS, m/z (%): 407 (M^+, 2), 226 (2), 165 (8), 121 (100), 105 (70), 77 (47); IR (Nujol): 1657, 1651, 1622, 1582, 1495, 1481, 1449, 1219, 1180, 1130, 1086, 1007, 960, 845, 829, 760, 715, 706, 690, 660, 645, 614 cm^{-1}.

*3.2.18. (Z)-2-(4-Cianophenylimino)-4,5-diphenyl-1,3-oxathiole (**3f**).* Yield 56%; crystallization from methanol gave white needles mp 140–141 °C. (Found: C, 74.25; H, 4.02; N, 7.87; S, 9.11. $C_{22}H_{14}N_2OS$ requires: C, 74.55; H, 3.98; N, 7.90; S, 9.05); ^{1}H NMR δ ($CDCl_3$, 200 MHz): 7.18–7.43 (m, 12H), 7.65 (d, 2H, J=8.51 Hz); ^{13}C NMR δ ($CDCl_3$, 50.4 MHz): 107.68, 113.53, 118.93, 121.95, 127.41, 127.72, 128.48, 128.95, 129.13, 129.20, 129.27, 129.47, 133.71, 142.32, 152.28, 162.24; MS, m/z (%): 354 (M^+, 2), 282 (1), 247 (1), 198 (1), 165 (9), 121 (100), 105 (80), 77 (48); IR (Nujol): 2231, 1650, 1623, 1596, 1499, 1446, 1221, 1175, 1131, 1089, 1072, 1032, 961, 860, 764, 747, 696, 691 cm^{-1}.

3.3. X-ray structure determination of compound 2g

Crystal data: $C_{30}H_{24}O_3S$, M_r=464.55, monoclinic, space group $P2_1/n$, a=11.1663 (8), b=12.1181 (11), c=18.2901 (12) Å, β=93.196 (5)°, U=2471.1 (3) Å^3 at −100 °C; Z=4, D_x=1.249 g cm^{-3}, $F(000)$=976, μ=0.16 mm^{-1}. *Data collection*: A colorless prism 0.54×0.42×0.19 mm was mounted in inert oil on a glass fiber and transferred to the cold gas stream of the diffractometer (Siemens P4). Measurements were performed to $2\theta_{max}$ 50° with monochromated Mo Kα radiation. Of 5193 measured reflections, 4350 were unique (R_{int}=0.033) and were used for all calculations. *Structure refinement*: The structures were refined anisotropically against F^2 (program SHELXL-97)[1] The hydrogen atoms were refined using rigid methyl groups or a riding model. The final *wR*2 value was 0.0898 for all reflections and 309 parameters, with *R*1 0.0417 for reflections with $I>2\sigma(I)$; max. $\Delta\rho$ 0.19 e/Å^3, S 0.85.

Complete crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre under the number CCDC 753391. Copies may be requested free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, England (e-mail: deposit@ccdc.cam.ac.uk).

3.4. X-ray structure determination of compound 3c

Crystal data: $C_{21}H_{13}Cl_2NOS$, M_r=398.28, triclinic, space group $P\bar{1}$, a=8.493 (2), b=9.925 (3), c=11.358 (3) Å, α=94.78 (2), β=97.72 (2),

γ=110.02 (2)°, U=882.8 (4) Å^3 at −130 °C; Z=2, D_x=1.498 g cm^{-3}, F (000)=408, μ=0.5 mm^{-1}. *Data collection*: A colorless tablet 0.7×0.4×0.2 mm was mounted in inert oil on a glass fiber and transferred to the cold gas stream of the diffractometer (Stoe STADI-4). Measurements were performed to $2\theta_{max}$ 50° with monochromated Mo Kα radiation. Of 3987 measured reflections, 3117 were unique (R_{int}=0.016) and were used for all calculations. *Structure refinement*: The structures were refined anisotropically against F^2 (program SHELXL-97).[64] Hydrogen atoms were included with a riding model. The final *wR*2 value was 0.0869 for all reflections and 235 parameters, with *R*1 0.0340 for reflections with $I>2\sigma(I)$; max. $\Delta\rho$ 0.26 e/Å^3, *S* 1.07.

Complete crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre under the number CCDC 243017. Copies may be requested free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, England (e-mail: deposit@ccdc.cam.ac.uk).

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Supplementary data

X-ray structural data of compounds **2g** and **3c** and several representative voltammograms. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2010.12.044.

References and notes

1. Stapelfeldt, H. E.; Perone, S. P. *Anal. Chem.* **1968**, *40*, 815.
2. Stapelfeldt, H. E.; Perone, S. P. *Anal. Chem.* **1969**, *41*, 623.
3. Johnson, D. C.; Gaines, P. R. *Anal. Chem.* **1973**, *45*, 1670.
4. Lund, H.; Simonet, J. *Bull. Soc. Chim. Fr.* **1973**, 1843.
5. Simonet, J.; Lund, H. *Bull. Soc. Chim. Fr.* **1975**, 2547.
6. Boujlel, K.; Simonet, J. *Tetrahedron Lett.* **1979**, 1497.
7. Adams, C.; Kamkar, N. M.; Utley, J. H. P. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1767.
8. Guirado, A.; Barba, F.; Manzanera, C.; Velasco, M. D. *J. Org. Chem.* **1982**, *47*, 142.
9. Guirado, A.; Barba, F.; Tévar, A. *Synth. Commun.* **1984**, *14*, 333.
10. Guirado, A.; Barba, F.; Hursthouse, M. B.; Arcas, A. *J. Org. Chem.* **1988**, *54*, 3205.
11. These compounds are sometimes also referred as isocyanide dichlorides, isonitrile dichlorides, carbylamine dichlorides, dichloromethyleneamines, or carbonyl dichloride imides.
12. Kuehle, E.; Anders, B.; Zumach, G. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 649.
13. Ulrich, H. *The Chemistry of Imidoyl Halides*; Plenum: New York, NY, 1968; Chapter 2.
14. Guirado, A.; Zapata, A.; Fenor, M. *Tetrahedron Lett.* **1992**, *33*, 4779.
15. Guirado, A.; Zapata, A.; Gómez, J. L.; Trabalón, L.; Gálvez, J. *Tetrahedron* **1999**, *55*, 9631.
16. Guirado, A.; Zapata, A.; Galvez, J. *Tetrahedron Lett.* **1994**, *35*, 2365.
17. Guirado, A.; Zapata, A.; Jones, P. G. *Tetrahedron* **1995**, *51*, 3641.
18. Guirado, A.; Zapata, A.; Andreu, R.; Ramirez de Arellano, C.; Jones, P. G.; Galvez, J. *Tetrahedron* **2009**, *65*, 3886.
19. Guirado, A.; Zapata, A.; Jones, P. G. *Tetrahedron* **1995**, *51*, 10375.
20. Bak, C.; Praefcke, K. *Chem. Ber.* **1979**, *112*, 2744.
21. Bak, C.; Praefcke, K. *J. Heterocycl. Chem.* **1980**, *17*, 1655.
22. Saville, B.; Steer, M. *J. Chem. Soc., Chem. Commun.* **1972**, 616.
23. De Mayo, P.; Weedon, A. C.; Wong, G. S. K. *J. Org. Chem.* **1979**, *44*, 1977.
24. Hartnedy, R. C.; Dittmer, D. C. *J. Org. Chem.* **1984**, *49*, 4752.
25. Bak, C.; Praefcke, K. *Chem. Ztg.* **1978**, *102*, 456.
26. Dittmer, D. C.; Kuhlmann, G. E. *J. Org. Chem.* **1970**, *35*, 4224.
27. Arbuzov, B. A.; Polezhaeva, N. A.; Smirnov, V. V.; Musina, A. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1975**, 1658.
28. Ohno, A. In *Organic Chemistry of Sulfur*; Oae, S., Ed.; Plenum: New York, NY, 1977, Chapter 5.
29. Guirado, A.; López-Sanchez, E.; Andreu, R.; Zapata, A. *Tetrahedron Lett.* **2004**, *45*, 2075.
30. Aitken, R. A.; Hill, L. In *Comprehensive Heterocyclic Chemistry II*; Katritzky, A., Rees, C., Scriven, E., Eds.; Pergamon: Oxford, 1996; Vol. 3, Chapter 3.10.
31. Aitken, R. A.; Power, L. A. In *Comprehensive Heterocyclic Chemistry III*; Katritzky, A., Ramsden, C., Scriven, E., Taylor, R., Eds.; Pergamon: Oxford, 2008; Vol. 4, Chapter 4.10.
32. Elliott, A. In *Comprehensive Heterocyclic Chemistry*; Katritzky, A., Rees, C., Eds.; Pergamon: Oxford, 1984; Vol. 6, Chapter 4.30.
33. Ref. 30, p 555.
34. Singh, H.; Ahuja, A. S.; Malhotra, N. *J. Chem. Soc., Perkin Trans. 1* **1982**, 653.
35. Ueno, Y.; Okawara, M. *Synthesis* **1979**, 182.
36. Roshchupkina, G. I.; Gatilov, Y. V.; Rybalova, T. V.; Reznikov, V. A. *Eur. J. Org. Chem.* **2004**, 1765.
37. Kulka, M. *Can. J. Chem.* **1981**, *59*, 1557.
38. Ishida, M.; Sugiura, K.; Takagi, K.; Hiraoka, H.; Kato, S. *Chem. Lett.* **1988**, 1705.
39. Ottmann, G.; Hooks, H. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 455.
40. Ottmann, G. F.; Vickers, G. D.; Hooks, H., Jr. *J. Heterocycl. Chem.* **1967**, *4*, 527.
41. Le Marechal, A.; Robert, A.; Leban, I. *J. Chem. Soc., Perkin Trans. 1* **1993**, 351.
42. Baudy, M.; Robert, A.; Foucaud, A. *J. Org. Chem.* **1978**, *43*, 3732.
43. L'Abbe, G.; Buelens, J.; Dehaen, W.; Toppet, S.; Van Meervelt, L. *J. Chem. Soc., Perkin Trans. 1* **1994**, 1263.
44. Ryan, M. D.; Evans, D. H. *J. Electroanal. Chem.* **1976**, *67*, 333.
45. Allen, F. H. *Acta Crystallogr.* **2002**, *B58*, 380.
46. Galvez, J.; Guirado, A. *J. Comput. Chem.* **2010**, *31*, 520.
47. Kessler, H. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 219.
48. Koepke, B.; Voss, J. *Chem. Ber.* **1982**, *115*, 2221.
49. Baudy, M.; Robert, A. *Tetrahedron Lett.* **1980**, *21*, 2517.
50. Merijanian, A.; Sharma, G. M.; Moushati, J.; Gunderson, K. *J. Org. Chem.* **1986**, *51*, 543.
51. Hirai, K. *Tetrahedron Lett.* **1971**, 1137.
52. Hirai, K.; Sugimoto, H.; Ishiba, T. *Tetrahedron* **1977**, *33*, 1595.
53. Hirai, K.; Ishiba, T. *J. Chem. Soc. D* **1971**, 1318.
54. Kim, J.; Kim, H.; Shin, Y.; Lee, C.; Won, C.; Lee, S.; Lee, J.; Kim, Y.; Kang, J.; Ye, S.; Chung, M. *Exp. Mol. Med.* **2008**, *40*, 514.
55. Kim, M.; Lee, H.; Roh, E.; Kim, B.; Chung, E.; Lee, Y.; Lee, I.; Lee, H.; Lee, C.; Han, S.; Kim, Y. *Biochem. Pharmacol.* **2008**, *76*, 373.
56. Kim, B.; Roh, E.; Lee, H.; Lee, I.; Ahn, B.; Jung, S.; Lee, H.; Han, S.; Kim, Y. *Mol. Pharmacol.* **2008**, *73*, 1309.
57. Yadav, L.; Tripathi, R.; Dwivedi, r.; Singh, H. *J. Agric. Food Chem.* **1992**, *40*, 1700.
58. Niki, T.; Ikeda, S.; Hayasaka, F. JP 2004217553, 2004.
59. Niki, T.; Mizukoshi, T.; Suzuki, H.; Hayasaka, F. JP 2004168706, 2004.
60. Kühle, E. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 647.
61. *Spartan'06*; Wavefunction: Irvine, CA, 2006.
62. A picture of a similar cell can be see: *Organic Electrochemistry*; Lund, H., Baizer, M. M., Eds.; Marcel Dekker: New York, NY, 1991; Chapter 6, p 264.
63. Caution must be exercised when handling perchlorates in order to exclude explosion risk. Evaporation of organic solutions containing perchlorates requires to be carried out in vacuo and at moderate temperature. The contact with strong acids must be avoided.
64. Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112.