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# Electrochemical synthesis of 2-arylimino-4,5-di(2-furyl)-1,3-dioxoles and (*E*)-1,2-di(2-furyl)vinylene bis(*N*-arylchloroformimidates). HF and B3LYP computational study of the topomerization mechanism of aryliminodioxoles

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ABSTRACT

Cathodic reductions of 2,2′-furils in the presence of *N*-arylcarbonimidoyl dichlorides lead to 2-arylimino-4,5-di(2-furyl)-1,3-dioxoles in high yields, along with minor amounts of (*E*)-1,2-di(2-furyl)vinylene bis(*N*-arylchloroformimidates). HF and B3LYP density functional theory methods have been applied to the determination of molecular geometries and to study the topomerization mechanism of aryliminodioxoles. The molecular structure of (*E*)-1,2-di(2-furyl)vinylene bis[*N*-(2-chloro-4-methylphenyl)chloroformimidate] has been determined by X-ray crystallography and compared with the calculated structure.


## 1. Introduction

Electrochemical reductions of benzil and other diaryl-1,2-diketones have been studied from various points of view. Reactions in protic media lead to benzoins, whose formation corresponds to a two-electron, two-proton process.[1–3] The interest in these reactions is mainly mechanistic. Electrolyses in aprotic media carried out in the presence of non-electroactive electrophilic reagents have synthetic utility and are of great interest since under these conditions electrogenerated intermediates can attack these reagents instead of undergoing simple protonation. Alkylations[4,5] in the presence of alkyl halides or alkyl tosylates and acylations[6–9] performed in the presence either acyl halides or acid anhydrides are standard reported reactions. Similar reductions were applied to monothiobenzils leading to (*Z*)-α-benzoyloxy-β-benzoylthiostilbenes.[10]

In the course of this synthetic strategy we established that carbonimidoyl dichlorides,[11] which are inexpensive and easily available reagents,[12,13] show optimal chemical and electrochemical properties that can be exploited synthetically. Thus, they were found to be reducible at relatively high cathodic potentials providing isocyanides in near quantitative yields,[14,15] but showed also a high tendency to act exclusively as geminal dielectrophilic agents, thereby capturing reactive intermediates generated by electroreduction of benzils or anils at relatively lower cathodic potentials, yielding 2-arylimino-4,5-diaryl-1,3-dioxoles[16,17] or 3,4,5-triaryl-2-aryliminooxazolines,[18] respectively. In order to expand this preparative methodology, we attempted the synthesis of 2-arylimino-4,5-diheteroaryl-1,3-dioxoles by electrochemical reduction of commercially available starting materials such as 2,2′-pyridil, 2,2′-thenil, bis(pyrrol-2-yl)-1,2-ethanedione and 2,2′-furils. In a preliminary communication we reported that the only successful experiments were those starting from furils,[19] whereas the other electrolyses led to isocyanides via indirect electroreduction of carbonimidoyl dichlorides present in the catholyte.[20]

In this paper we report full details of the electrosynthesis of a new family of dioxole derivatives formed by electroreduction of 2,2′-furils **1** in the presence of carbonimidoyl dichlorides.[21] These substances were generated along with minor amounts of compounds that have been identified as a new class of formimidate derivatives whose structure has been corroborated by X-ray crystallography. As in the case of electrolysis products derived from

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benzils, the NMR spectra of the prepared aryliminodioxoles exhibit a notable dependence upon temperature that is attributable to a topomerization process whose mechanism has been now studied by HF and B3LYP density functional theory methods.

## 2. Results and discussion

2,2′-Furils **1** were reduced at constant cathodic potentials in the presence of equimolar amounts of arylcarbonimidoyl dichlorides **2** (Scheme 1). After a short time the colour of the catholyte, initially yellow, turned to purple. When the current was interrupted the solutions became yellow again. This observation was repeated throughout the electrolysis. The electricity consumption was 2 F/mol of **1**. After each preparative electrolysis the crude products were precipitated by mixing the catholyte solutions with cold water, after which they could easily be isolated and purified by extraction and fractional crystallization. The main reaction products were obtained in good yields (Table 1) and were identified by IR, MS, NMR spectroscopy and elemental analysis as the corresponding 2-arylimino-4,5-di(2-furyl)-1,3-dioxoles **3**. Electrolyses in the presence of alkylcarbonimidoyl dichlorides ($PhCH_2CH_2N{=}CCl_2$ and $C_6H_{11}N{=}CCl_2$) were also carried out. However, these reactions were unsuccessful, leading to a complex mixture of unidentified products. The chemistry of various classes of 1,3-dioxoles has been studied for a long time.[17] However, with the exception of the electrochemical method, only one preparative procedure for 2-imino derivatives has been reported, with only two reaction examples and remarkably different yields, and requiring a complex and expensive protocol that involves the prior synthesis of bis(tributylstannyloxy)ethenes followed by reaction with isothiocyanates.[22]

Ascorbic acid ($E_{1/2}$=0.18 V vs Ag/AgCl) and further free enediols are substances having low oxidation potentials and a pronounced antioxidant activity.[23] However, enediol iminocarbonate **3a** shows a relatively high reluctance to be oxidized ($E_{1/2}$=1.03 V vs SCE) at the same working electrode. Owing to the recent nature of the development of our synthetic methodology, possible applications of products of type 3 remain scarcely investigated. These have been found to be hydrolyzable providing dioxolenones without need for phosgene reactions.[17] Nucleophilic attack, polymerization, photochemical and electrochemical reactions seem to be interesting fields to be explored.

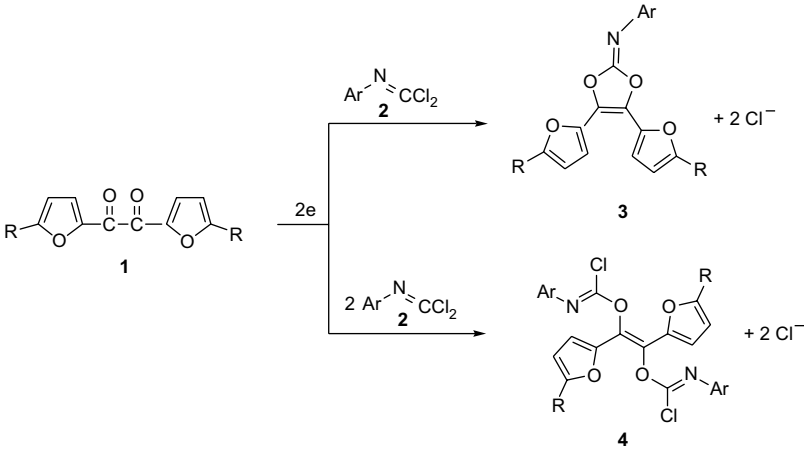
Minor electrolysis products were also isolated or detected in trace amounts; structures were determined by the usual spectroscopic techniques and confirmed by X-ray crystallography as a new class of compounds: (*E*)-1,2-di(2-furyl)vinylene bis(*N*-arylchloroformimidates) **4**. The course of electrolyses varying the ratio of 2 (double or a half amount) was checked by TLC, showing no significant differences. The molecule of **4f** (Fig. 1) displays crystallographic inversion symmetry. Consistent with this, the geometry at the central double bond is confirmed as trans. The interplanar angle between the phenyl and furanyl rings is 60.4°. There are two notably wide $sp^2$ bond angles, namely C5#–C5–C1 129.7(4)° and C2–C1–C5 131.5(5)°, but a search of the Cambridge Database[24] revealed that this is normal for the group C=C-(2-furanyl), with corresponding average values of 127.8° and 132.3°, respectively, for 50 hits and 63 individual values.

**Table 1**
Results of electrochemical reductions of furils **1** in the presence of carbonimidoyl dichlorides **2**

| | Ar | R | **3** (yield %) | **4** (yield %) |
|---|---|---|---|---|
| **a** | $C_6H_5$ | H | 74 | 8 |
| **b** | 4-$ClC_6H_4$ | H | 76 | 12 |
| **c** | 2,4-$Cl_2C_6H_3$ | H | 73 | 11 |
| **d** | 4-$NCC_6H_4$ | H | 73 | 11 |
| **e** | 4-$BrC_6H_4$ | H | 74 | 13 |
| **f** | 2-Cl-4-$CH_3C_6H_3$ | H | 76 | 10 |
| **g** | $C_6H_5$ | $CH_3$ | 75 | Traces |
| **h** | 4-EtOOC-$C_6H_4$ | $CH_3$ | 75 | Traces |
| **i** | 2-Cl-4-$CH_3C_6H_3$ | $CH_3$ | 73 | Traces |
| **j** | 2,4-$Cl_2C_6H_3$ | $CH_3$ | 74 | Traces |
| **k** | 4-$BrC_6H_4$ | $CH_3$ | 67 | Traces |
| **l** | 4-Cl-2-$CH_3C_6H_4$ | $CH_3$ | 70 | Traces |

Consistent with our proposal for the electrogeneration of 2-arylimino-1,3-dioxoles derived from benzils,[17] the formation of products **3** can be explained on the basis of electrogeneration of two nucleophilic centres that are geminally captured by the non-electroactive dielectrophilic reagents present in the catholyte. The formation of products **4** can be similarly explained, but with the participation of two independent dielectrophilic molecules for configurational reasons. It should be noted that the formation of compounds similar to products **4** was not observed during electroreductions of benzils.

NMR spectroscopy of products **3** showed remarkable temperature dependence. Assignments of spectra were made by DEPT; H,C-COSY and selective decoupling techniques. As is reported in the Experimental section, carbons pertaining to aryl groups attached to nitrogen are labelled 1″-4″ or 1-6″ depending on symmetry, whereas the carbons of furyl groups supported by the dioxole ring are denoted as 2-5 and 2′-5′. $^{13}C$ NMR spectra recorded at ambient temperature were inconsistent in the number of signals with respect to configurationally stable compounds, but a moderate




**Scheme 1.**

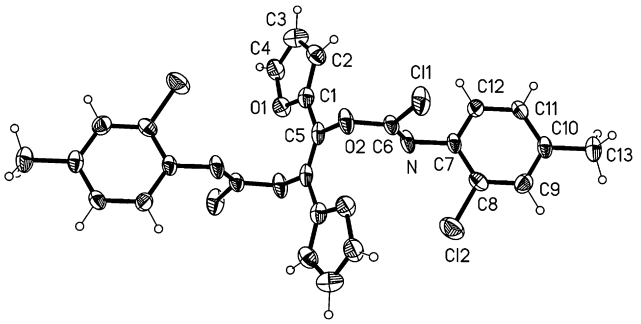
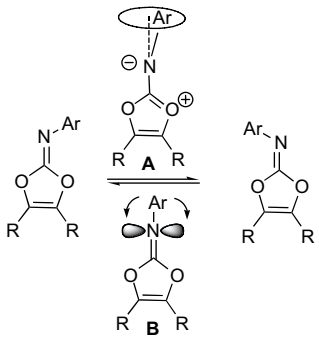



**Figure 1.** The structure of the major disorder component of **4f** in the solid state, with thermal ellipsoids shown at 50% probability.

increase of temperature lowered this number to that expected for non-configurationally stable substances. However, spectra at low temperature provided almost the number of peaks predicted for compounds with total configurational stability. $^1$H NMR spectra were also highly temperature dependent.

In a previous paper[17] NMR spectra of 2-arylimino-4,5-diaryl-1,3-dioxoles at different temperatures demonstrated geometrical interconversions involving a relatively low configurational stability around the carbon–nitrogen double bond. In general, these facts have been explained by two opposite models, called either 'rotation' or 'inversion' mechanisms.[25] The rotation mechanism is conceived as involving a polar transition state with loss of the carbon–nitrogen double bond following an 'out-of-plane' fluctuation (Scheme 2, TS **A**, torsion angle 90°). Conversely, the alternative inversion mechanism implies rehybridization of the non-bonded electron pair at nitrogen to a p orbital, with the carbon–nitrogen double bond character remaining unaffected, in this way following an 'in-plane' molecular fluctuation (Scheme 2, TS **B**).

To gain insight into the mechanism operating with compounds **3**, a computational study on the predictions of both models was performed at the B3LYP/6-311++G(d,p)//B3LYP/6-31G(d) level of theory.[26] A summary of the results obtained for compound **3a** is displayed in Figure 2. Thus, panel A shows the energy profile for the molecule structures related to the torsional motion about the double bond C=N that occurs during the rotation mechanism. Energy values are given relative to the most stable molecule (OCNC dihedral angle ≈0°, CNC angle=125.35°), and the profile was generated by modifying the OCNC torsion angle with the initial CNC angle constraint applied to all structures. Panel B shows the corresponding energy profile for the inversion mechanism, which was generated by modifying the CNC angle without further constraints (during this motion the OCNC dihedral angle remains ≈0° for all molecule structures). From Figure 2 it follows that both profiles show an energy maximum, which is attained at an OCNC torsion angle=90° (Panel A) and for a CNC angle=180° (Panel B). Note,




**Scheme 2.**

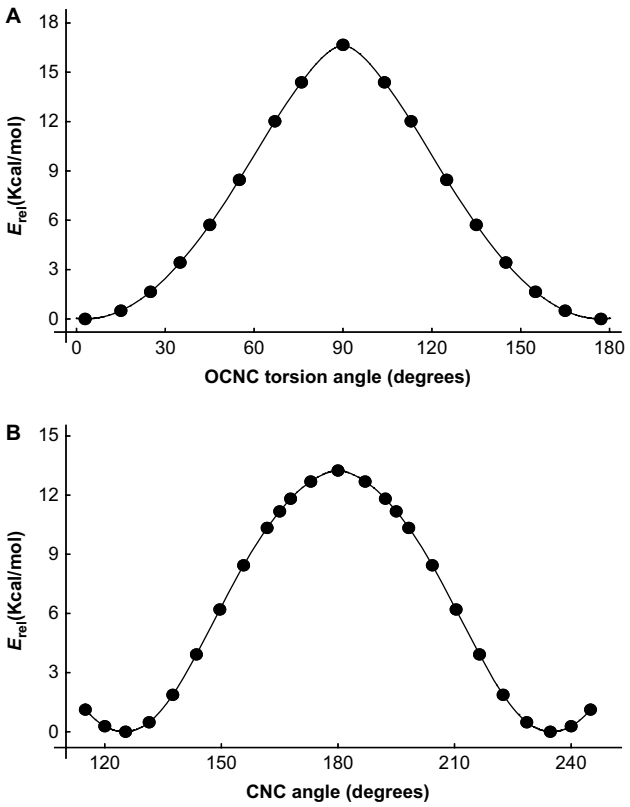



**Figure 2.** Panel A: Energy profile of the molecular interconversion according to the rotational mechanism. This profile was generated by modifying the OCNC torsion angle and with the constraint CNC angle=125.35° applied to all structures. Panel B: Energy profile for the inversion mechanism. The CNC angle was modified without further constraints. Energy values are relative to the most stable molecule configuration. Calculations were performed at the B3LYP/6-311++G(d,p)//B3LYP/6-31G(d) level of theory.

however, that the maximum for the inversion mechanism is 3.5 kcal/mol lower than for rotation. This implies that the mechanism for the topomerization of these compounds mainly involves an 'in-plane' inversion process. This was confirmed by obtaining the transition state (TS) optimized structure, which was determined without applying any constraints at the B3LYP/6-31G(d) level and characterized by vibrational frequency calculations that gave a sole imaginary frequency for the TS structure. The CNC angle in the TS was 173.4° revealing that there is a small deviation from the inversion mechanism in favour of the rotational one. In this context, if we remove the constraints from the molecule structure for the maximum energy in the rotation mechanism (Panel A, Fig. 3 CNC angle=125.35°), that configuration spontaneously reverts to the TS structure for the inversion process in which the CNC angle=173.35°. Also, it is interesting to note that the aryl group, which is almost coplanar with the dioxole ring during the inversion motion, changes its configuration to orthogonal in the transition state. This effect can be attributed to a gain of stabilization by orbital overlapping and also by lessening of steric hindrance (Scheme 3).

Figure 3 illustrates another key feature of the inversion mechanism, viz. the continuous shortening of the bond length C=N as the transition state is reached (a similar shortening was also found for the nitrogen–aryl bond, data not shown). Finally, the energy barrier (=$E_a$) for the inversion process was determined as the difference between the total molecular energy of the transition state TS and that of the global minimum of the reactant. The value of $E_a$ including ZPE and thermal corrections obtained at the same level as geometry optimizations was small, just 11.54 kcal/mol, whereas the value of $\Delta G^{\neq}_{298}$ is 13.05 kcal/mol.[27]

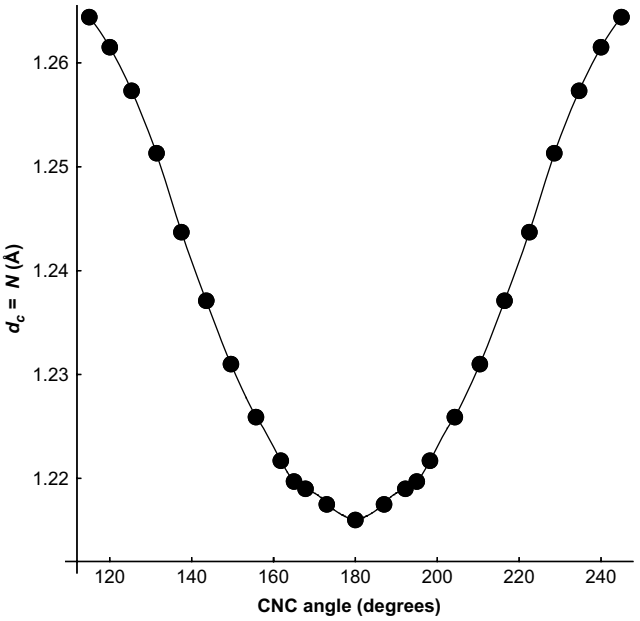
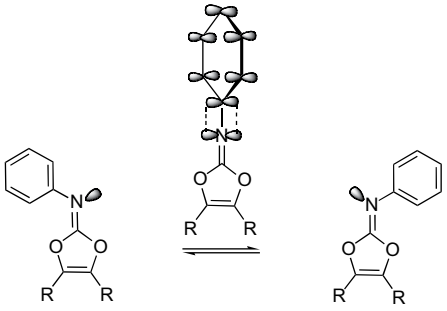



**Figure 3.** Variation of the C=N bond length as a function of the CNC angle for the inversion process. Other conditions as in Figure 1, Panel A.

The accuracy of the computational methodology applied to envisage molecular geometries was checked by comparing experimental X-ray crystallography data and the calculated molecular structure of **4f**. The results obtained are shown in Table 2 for bond lengths and bond angles and in Table 3 for selected dihedral angles. A good agreement was found, with differences in bond lengths ≈0.02Å and in bond angles ≈1° (Table 2). As expected, these differences are a little larger for dihedral angles (Table 3). This is a well known fact that has been ascribed to molecular distortion in the crystal structure induced by packing effects. Also, and in accordance with the previous theoretical analysis, data from Table 2 provide support for the view that a rotation mechanism is not involved in the topomerization process. The C=N double bond lengths found in the X-ray structure of 2-(2-chloro-4-methylphenylimino)-4,5-diphenyl-1,3-dioxole[17] (1.254(2) Å; cf. standard[28] C($sp^2$) –C=N–C bond length of 1.279 Å) and also in the optimized structure[29] for **3a** (1.257 Å) are unusually short. However, these bonds might be expected to be longer if the molecular interconversion process takes place through a polar mechanism since, under these conditions, the double bond character of the C3–N bond is lost.

To conclude, it has been established that cathodic reduction of difuryl-1,2-diketones carried out in the presence of carbonimidoyl dichlorides has a specific use for preparing previously inaccessible 2-arylimino-4,5-di(2-furyl)-1,3-dioxoles **3** and (*E*)-1,2-di(2-furyl)-vinylene bis(*N*-arylchloroformimidates) **4**. NMR spectra of 2-arylimino-1,3-dioxoles show a remarkable temperature dependence, which is attributable to a configurational instability according to an inversion process with a relatively low activation barrier that has been calculated to be about 11 kcal/mol.




**Scheme 3.**

**Table 2**
Selected bond lengths and bond angles of crystal and calculated structures in crystal structure of **4f** and their differences

| Bond | Crystal structure (Å) | Calculated structure[a] (Å) | Δ (Å) | Calculated structure[b] (Å) | Δ (Å) |
|---|---|---|---|---|---|
| N–C(6) | 1.235(3) | 1.252 | −0.017 | 1.232 | 0.003 |
| N–C(7) | 1.425(3) | 1.401 | 0.024 | 1.404 | 0.021 |
| O(2)–C(6) | 1.356(3) | 1.350 | 0.006 | 1.329 | 0.027 |
| O(2)–C(5) | 1.431(3) | 1.404 | 0.027 | 1.380 | 0.051 |
| C(5)–C(5)#1 | 1.316(8) | 1.356 | −0.030 | 1.326 | −0.010 |
| C(5)–C(1) | 1.455(5) | 1.443 | 0.012 | 1.457 | −0.002 |
| C(1)–C(2) | 1.346(7) | 1.377 | −0.031 | 1.349 | −0.003 |
| C(1)–O(1) | 1.382(6) | 1.369 | 0.013 | 1.344 | 0.038 |
| Cl(1)–C(6) | 1.725(2) | 1.771 | −0.046 | 1.735 | −0.010 |
| Cl(2)–C(8) | 1.742(2) | 1.755 | −0.013 | 1.741 | 0.001 |
| **Bond angle** | **Crystal structure (°)** | **Calculated structure[a] (°)** | **Δ (°)** | **Calculated structure[b] (°)** | **Δ (°)** |
| C(6)–O(2)–C(5) | 116.88(18) | 117.90 | −1.02 | 119.02 | −2.14 |
| C#(5)1–C(5)–O(2) | 115.0(4) | 118.05 | −3.05 | 119.01 | −4.01 |
| C#(5)1–C(5)–C(1) | 129.7(4) | 129.45 | 0.25 | 128.51 | 1.19 |
| O(2)–C(5)–C(1) | 115.2(3) | 112.29 | 2.91 | 112.29 | 2.91 |
| O(2)–C(5)–O(1) | 109.9(4) | 109.56 | 0.34 | 110.20 | −0.30 |
| C(2)–C(1)–C(5) | 131.5(5) | 130.16 | 1.34 | 129.68 | 1.82 |
| C(4)–C(3)–C(2) | 106.7(4) | 106.21 | 0.49 | 105.62 | 1.08 |
| C(3)–C(4)–O(1) | 110.5(4) | 110.55 | −0.05 | 110.77 | −0.27 |
| N–C(6)–O(2) | 124.6(2) | 124.92 | −0.32 | 124.56 | 0.04 |
| N–C(6)–Cl(1) | 127.40(18) | 127.23 | 0.17 | 126.57 | 0.83 |

[a] Geometry optimized at the B3LYP/6-31G(d) level of theory.
[b] Geometry optimized at the HF/6-31G(d) level of theory.

## 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. Electrochemical experiments were

**Table 3**
Selected dihedral angles of crystal and calculated structures of **4f** and their differences

| Dihedral angle | Crystal structure (°) | Calculated structure[a] (°) | Δ (°) | Calculated structure[b] (°) | Δ (°) |
|---|---|---|---|---|---|
| C(6)–O(2)–C(5)–C(5)#1 | 90.2(4) | 92.62 | −2.42 | 94.22 | −4.02 |
| C(6)–O(2)–C(5)–C(1) | −93.6(4) | −92.24 | −1.36 | −90.29 | −3.31 |
| C#(5)1–C(5)–C(1)–C(2) | 177.4(6) | 172.65 | 4.75 | 168.09 | 9.31 |
| O(2)–C(5)–C(1)–C(2) | 1.8(8) | 1.80 | 0.00 | 6.86 | −5.06 |
| C(5)#1–C(5)–C(1)–O(1) | −5.2(8) | −7.52 | 2.32 | −11.83 | 6.63 |
| O(2)–C(5)–C(1)–O(1) | 179.2(4) | 178.03 | 1.17 | 173.21 | 5.99 |
| C(2)–C(1)–O(1)–C(4) | −2.7(7) | −0.06 | −2.64 | −0.05 | −2.65 |
| C(5)–C(1)–O(1)–C(4) | 179.3(5) | 179.92 | −0.62 | 179.89 | −0.59 |
| C(5)–C(1)–C(2)–C(3) | 178.9(5) | 179.80 | −0.90 | 179.95 | −1.05 |
| C(1)–C(2)–C(3)–C(4) | 0.6(8) | 0.12 | 0.48 | 0.09 | 0.51 |
| C(7)–N–C(6)–O(2) | 179.0(2) | 176.51 | 2.49 | 177.37 | 1.63 |
| C(7)–N–C(6)–Cl(1) | −0.3(4) | −4.05 | 3.75 | −2.07 | 1.77 |
| C(5)–O(2)–C(6)–N | −6.9(4) | −2.70 | −4.20 | −2.81 | −4.09 |
| N–C(7)–C(8)–C(9) | 178.4(2) | 175.78 | 2.62 | 176.37 | 2.03 |
| C(12)–C(7)–C(8)–Cl(2) | 179.85(17) | 179.27 | 0.58 | 178.97 | 0.88 |

[a] Geometry optimized at the B3LYP/6-31G(d) level of theory.
[b] Geometry optimized at the HF/6-31G(d) level of theory.

performed with an Amel 552 potentiostat coupled to an Amel 721 integrator. Carbonimidoyl dichlorides **2** were prepared by standard procedures.[12]

All computations were performed with the Spartan'06 package program.[30] 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 and density functional theory calculations of geometry optimizations at the Hartree–Fock and B3LYP 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. Single-point energies were calculated with the 6-311++G(d,p) basis.

### 3.2. Electrolysis procedure

The electrochemical generation of products **3** and **4** was performed following the experimental procedure previously reported.[10,31,32] Compounds **1** (5 mmol) were electrolyzed under nitrogen atmosphere, in the presence of reagents **2** (5 mmol), at the following cathodic potentials: −0.80 V versus SCE (**1b**,**d**); −0.90 V (**1c**,**h**,**f**,**i**,**j**,**l**); −1.05 V (**1a**,**e**,**g**); −1.10 (**1k**). These potentials were selected in order to provide operative current intensities. The duration of the electrolyses ranged from 1.3 to 1.5 h. The average current intensities were close to 12 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/mol 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 ether layers were washed with cold water and dried on anhydrous magnesium sulfate. A solid mixture of reaction products was obtained by removing ether under reduced pressure. Then these were isolated in high purity by fractional crystallization from acetonitrile. Products **4** crystallized at room temperature, whereas crystallization of products **3** occurred at −10 °C from acetonitrile or petroleum ether.

#### 3.2.1. 2-Phenylimino-4,5-di(2-furyl)-1,3-dioxole (**3a**)

Yield 74%; crystallization from petroleum ether gave yellow needles, mp 125–127 °C. (Found: C, 69.53; H, 3.81; N, 4.80; $C_{17}H_{11}NO_4$ requires: C, 69.62; H, 3.78; N, 4.78); $^1$H NMR $\delta$ ($CDCl_3$, 200 MHz): 6.53 (br s, 2H, H-4,4′), 6.88 (d, 2H, $J$=3.5, H-3,3′), 7.12 (t, 1H, $J$=6.8, H-4″), 7.24–7.37 (m, 4H, H-2″,3″), 7.54 (br s, 2H, H-5,5′); $^{13}$C NMR $\delta$ ($CDCl_3$, 50.3 MHz): 111.10 (C-3,3′), 111.90 (C-4,4′), 123.31 (C-2″), 124.17 (C-4″), 128.84 (br, C-2,2′), 128.99 (C-3″), 140.49 (br, O–C═C–O), 143.41 (C-1″), 144.06 (C-5,5′), 148.78 (C═N–); MS $m/z$ (%): 293 ($M^+$, 5), 146 (22), 119 (55), 118 (100), 95 (55), 92 (30), 91(29), 90 (27), 64 (23), 63 (22); IR (Nujol): 3184, 1748, 1676, 1595, 1273, 1213, 1164, 1083, 1005, 955, 820, 783, 750, 696, 691 cm$^{-1}$.

#### 3.2.2. 2-(4-Chlorophenylimino)-4,5-di(2-furyl)-1,3-dioxole (**3b**)

Yield 76%; crystallization from acetonitrile gave brown flakes, mp 138–140 °C. (Found: C, 62.38; H, 3.11; N, 4.32. $C_{17}H_{10}ClNO_4$ requires: C, 62.30; H, 3.08; N, 4.27); $^1$H NMR $\delta$ ($CDCl_3$, 200 MHz): 6.55 (br s, 2H, H-4,4′), 6.89 (d, 2H, $J$=3.1, H-3,3′), 7.21 (d, 2H, $J$=8.5, H-2″), 7.28 (d, 2H, $J$=8.5, H-3″), 7.56 (br s, 2H, H-5,5′); $^{13}$C NMR $\delta$ ($CDCl_3$, 50.3 MHz): 111.20 (C-3,3′), 111.93 (C-4,4′), 124.65 (C-2″), 129.00 (C-3″), 129.30 (C-4″), 140.15, 140.42 (O–C═C–O), 142.05 (C-1″), 144.14 (C-5,5′), 149.07 (C═N–); MS $m/z$ (%): 329 ($M^+$+2, 17), 327 ($M^+$, 35), 153 (37), 118 (100), 95 (77), 92 (37), 90 (57), 89 (41), 63 (36); IR (Nujol): 3148, 1729, 1671, 1489, 1456, 1165, 1094, 954, 829, 742 cm$^{-1}$.

#### 3.2.3. 2-(2,4-Dichlorophenylimino)-4,5-di(2-furyl)-1,3-dioxole (**3c**)

Yield 73%; crystallization from acetonitrile gave pale yellow needles, mp 132–134 °C. (Found: C, 56.47; H, 2.52; N, 3.93. $C_{17}H_9Cl_2NO_4$ requires: C, 56.38; H, 2.50; N, 3.87); $^1$H NMR $\delta$ ($CDCl_3$, 300 MHz): 6.55 (br s, 2H, H-4,4′), 6.90 (d, 2H, $J$=3.3, H-3,3′), 7.25–7.33 (m, 2H, H-5″,6″), 7.43 (m, 1H, H-3″), 7.57 (br s, 2H, H-5,5′); $^{13}$C NMR $\delta$ ($CDCl_3$, 75.4 MHz): 111.44 (C-3,3′), 111.99 (C-4,4′), 124.43 (C-6″), 127.50 (C-5″), 128.60 (C-2,2′), 129.11 (C-2″), 129.36 (C-4″), 129.64 (C-3″), 140.10 (br, O–C═C–O), 140.24 (C-1″), 144.25 (C-5,5′), 149.83 (C═N–); MS $m/z$ (%): 363 ($M^+$+2, 34), 361 ($M^+$, 66), 187 (24), 146 (39), 118 (100), 95 (50), 92 (31), 90 (31), 89 (43), 63 (22); IR (Nujol): 1827, 1729, 1682, 1651, 1593, 1516, 1383, 1217, 1102, 1019, 872, 760 cm$^{-1}$.

#### 3.2.4. 2-(4-Cyanophenylimino)-4,5-di(2-furyl)-1,3-dioxole (**3d**)

Yield 73%; crystallization from petroleum ether gave pale yellow needles, mp 135–136 °C. (Found: C, 67.99; H, 3.23; N, 8.75. $C_{18}H_{10}N_2O_4$ requires: C, 67.92; H, 3.17; N, 8.80); $^1$H NMR $\delta$ ($CDCl_3$, 300 MHz): 6.57 (m, 2H, H-4,4′), 6.92 (d, 2H, $J$=3.6, H-3,3′), 7.34 (d, 2H, $J$=8.4, H-2″), 7.59–7.64 (m, 4H, $J$=8.5, H-3,3′,3″); $^{13}$C NMR $\delta$ ($CDCl_3$, 50.3 MHz): 107.12 (C-4″), 111.39 (C-3,3′), 112.04 (C-4,4′), 119.16 (CN), 124.00 (C-2″), 128.90 (C-2,2′), 133.06 (C-3″), 139.76 (O–C═C–O), 144.26 (C-5,5′), 147.88 (C-1″), 149.82 (C═N–); MS $m/z$ (%): 318 ($M^+$, 8), 146 (19), 118 (100), 95 (52), 92 (29), 90 (30), 89 (43), 63 (20); IR (Nujol): 3155, 2223, 1746, 1723, 1675, 1601, 1502, 1273, 1221, 1161, 1084, 1011, 954, 843, 739 cm$^{-1}$.

#### 3.2.5. 2-(4-Bromophenylimino)-4,5-di(2-furyl)-1,3-dioxole (**3e**)

Yield 75%; crystallization from acetonitrile gave pale brown needles, mp 138–141 °C. (Found: C, 54.88; H, 2.66; N, 3.83. $C_{17}H_{10}BrNO_4$ requires: C, 54.86; H, 2.71; N, 3.76); $^1$H NMR $\delta$ ($CDCl_3$, 300 MHz, +25 °C): 6.55 (br s, 2H, H-4,4′), 6.89 (d, 2H, $J$=3.0, H-3,3′), 7.16 (d, 2H, $J$=8.7, H-2″), 7.44 (d, 2H, $J$=8.7, H-3″), 7.56 (br s, 2H, H-5,5′); $^1$H NMR $\delta$ ($CDCl_3$, 300 MHz, +60 °C): 6.52 (dd, 2H, $J$=3.4, 1.8, H-4,4′), 6.86 (dd, 2H, $J$=3.3, 0.6, H-3,3′), 7.14 (d, 2H, $J$=8.7, H-2″), 7.42 (d, 2H, $J$=8.7, H-3″), 7.54 (dd, 2H, $J$=1.7, 0.6, H-5,5′); $^1$H NMR $\delta$ ($CDCl_3$, 300 MHz, −60 °C): 6.59 (m, 2H, H-4,4′), [6.88 (d, 1H, $J$=3.3), 7.02 (d, 1H, $J$=3.3), H-3,3′], 7.22 (d, 2H, $J$=8.4, H-2″), 7.47 (d, 2H, $J$=8.4, H-3″), [7.60 (br s, 1H), 7.62 (br s, 1H), H-5,5′]; $^{13}$C NMR $\delta$ ($CDCl_3$, 75.4 MHz, +25 °C): 111.09 (C-3,3′), 111.83 (C-4,4′), 116.94 (C-4″), 124.96 (C-2″), 128.76 (br, C-2-2′), 131.85 (C-3″), [139.94, 140.26 (O–C═C–O)], 142.43 (C-1″), 144.03 (C-5,5′), 148.95 (C═N–); $^{13}$C NMR $\delta$ ($CDCl_3$, 75.4 MHz, +60 °C): 111.18 (C-3,3′), 111.80 (C-4,4′), 116.99 (C-4″), 125.00 (C-2″), 128.96 (C-2-2′), 131.91 (C-3″), 140.32 (O–C═C–O), 142.72 (C-1″), 144.08 (C-5,5′), 148.94 (C═N–); $^{13}$C NMR $\delta$ ($CDCl_3$, 75.4 MHz, −60 °C): [110.78, 110.89 (C-3,3′)], [111.85, 111.90 (C-4,4′)], 116.79 (C-4″), 124.84 (C-2″), [127.89, 128.18 (C-2,2′)], 131.65 (C-3″), [139.26, 139.83 (O–C═C–O)], 141.62 (C-1″), [143.83, 143.98 (C-5,5′)], 148.88 (C═N–); MS $m/z$ (%): 373 ($M^+$+2, 3), 371 ($M^+$, 3), 146 (18), 118 (100), 95 (53), 92 (31), 90 (60), 63 (38); IR (Nujol): 1728, 1672, 1488, 1271, 1166, 1097, 1007, 953, 826, 742 cm$^{-1}$.

#### 3.2.6. 2-(2-Chloro-4-methylphenylimino)-4,5-di(2-furyl)-1,3-dioxole (**3f**)

Yield 75%; crystallization from acetonitrile gave orange needles, mp 118–120 °C. (Found: C, 63.14; H, 3.51; N, 4.03. $C_{18}H_{12}ClNO_4$ requires: C, 63.26; H, 3.54; N, 4.10); $^1$H NMR $\delta$ ($CDCl_3$, 200 MHz): 2.30 (s, 3H, $CH_3$), 6.52 (br s, 2H, H-4,4′), 6.86 (d, 2H, $J$=3.3, H-3,3′), 7.03 (dd, 1H, $J$=7.9, 1.6, H-5″), 7.17 (d, 1H, $J$=8.1, H-6″), 7.23 (d, 1H, $J$=1.4, H-3″), 7.53 (br s, 2H, H-5,5′); $^{13}$C NMR $\delta$ ($CDCl_3$, 50.3 MHz): 20.60 ($CH_3$), 111.18 (C-3,3′), 111.85 (C-4,4′), 123.26 (C-6″), 127.32 (C-2″), 127.95 (C-5″), 128.93 (C-2,2′), 130.21 (C-3″), 134.71 (C-4″), 138.62 (C-1″), 140.23 (O–C═C–O), 144.05 (C-5,5′), 149.33 (C═N–); MS $m/z$ (%): 341 ($M^+$, 65), 218 (15), 167 (35), 146 (45), 132 (53), 118 (100), 95 (55); IR (Nujol): 3108, 1740, 1686, 1495, 1466, 1267, 1209, 1162, 1055, 958, 818, 752 cm$^{-1}$.

#### 3.2.7. 2-Phenylimino-4,5-bis(5-methyl-2-furyl)-1,3-dioxole (**3g**)

Yield 75%; crystallization from petroleum ether gave pale yellow needles, mp 129–131 °C. (Found: C, 69.97; H, 4.69; N, 4.32.

$C_{19}H_{15}NO_4$ requires: C, 71.02; H, 4.71; N, 4.36); $^1$H NMR $\delta$ ($CDCl_3$, 200 MHz, +25 °C): 2.37 (s, 6H, $CH_3$, $CH_3'$), 6.13 (br s, 2H, H-4,4′), 6.73 (br s, 2H, H-3,3′), 7.10–7.15 (m, 1H, H-4″), 7.25–7.38 (m, 4H, H-2″,3″); $^1$H NMR $\delta$ ($CDCl_3$, 300 MHz, −60 °C): [2.40 (s, 3H), 2.41 (s, 3H), $CH_3$, $CH_3'$], 6.18 (m, 2H, H-4,4′), [6.75 (d, 1H, $J$=3.6), 6.84 (d, 1H, $J$=3.3), H-3,3′], 7.20 (t, 1H, $J$=7.2, H-4″), 7.35–7.46 (m, 4H, H-2″,3″); $^{13}$C NMR $\delta$ ($CDCl_3$, 50.3 MHz, +25 °C): 13.63 ($CH_3$), 107.98 (C-4,4′), 111.65 (C-3,3′), 123.27 (C-2″), 123.88 (C-4″), 128.09 (br, C-2,2′), 128.84 (C-3″), 138.78 (br, O–C═C–O), 143.53 (C-1″), 149.02 (C═N–), 154.06 (C-5,5′); $^{13}$C NMR $\delta$ ($CDCl_3$, 75.4 MHz, −60 °C): [13.87, 13.90 ($CH_3$, $CH_3'$)], [107.97, 107.99 (C-4,4′)], [111.20, 111.34 (C-3,3′)], 123.10 (C-2″), 123.87 (C-4″), [127.25, 127.54 (C-2,2′)], 128.84 (C-3″), [137.93, 138.40 (O–C═C–O)], 142.76 (C-1″), 148.99 (C═N–), [153.86, 153.94 (C-5,5′)]; MS $m/z$ (%): 321 ($M^+$, 30), 184 (100), 109 (13), 77 (20); IR (Nujol): 1739, 1669, 1597, 1464, 1275, 1208, 1118, 1019, 781, 698 cm$^{-1}$.

### 3.2.8. 2-(4-Ethoxycarbonylphenylimino)-4,5-bis(5-methyl-2-furyl)-1,3-dioxole (**3h**)

Yield 75%; crystallization from acetonitrile gave pale yellow needles, mp 136–138 °C. (Found: C, 67.30; H, 4.90; N, 3.61. $C_{22}H_{19}NO_6$ requires: C, 67.17; H, 4.87; N, 3.56); $^1$H NMR $\delta$ ($CDCl_3$, 300 MHz): 1.39 (t, 3H, $J$=7.2, $CH_3$), 2.38 (s, 6H, $CH_3$, $CH_3'$), 4.38 (q, 2H, $J$=7.2, $CH_2$), 6.14 (br s, 2H, H-4,4′), 6.74 (br s, 2H, H-3,3′), 7.32 (d, 2H, $J$=8.4, H-2″), 8.04 (d, 2H, $J$=8.4, H-3″); $^{13}$C NMR $\delta$ ($CDCl_3$, 75.4 MHz): 13.57 ($CH_3$, $CH_3'$), 14.26 ($CH_3$), 60.60 ($CH_2$), 108.02 (C-4,4′), 111.82 (C-3,3′), 123.06 (C-2″), 125.77 (C-4″), 128.19 (br, C-2,2′), 130.50 (C-3″), 138.40 (br, O–C═C–O), 148.10 (C-1″), 149.70 (C═N–), 154.23 (C-5,5′), 166.38 (C═O); MS $m/z$ (%): 393 ($M^+$, 30), 174 (100), 159 (66), 146 (29), 131 (16), 109 (18); IR (Nujol): 1738, 1712, 1669, 1603, 1464, 1456, 1368, 1284, 1245, 1210, 1115, 1025, 968, 787, 702 cm$^{-1}$.

### 3.2.9. 2-(2-Chloro-4-methylphenylimino)-4,5-bis(5-methyl-2-furyl)-1,3-dioxole (**3i**)

Yield 73%; crystallization from petroleum ether gave orange needles, mp 119–120 °C. (Found: C, 65.00; H, 4.28; N, 3.83. $C_{20}H_{16}ClNO_4$ requires: C, 64.96; H, 4.36; N, 3.79); $^1$H NMR $\delta$ ($CDCl_3$, 300 MHz): 2.31 (s, 3H, $CH_3$), 2.37 (s, 6H, $CH_3$, $CH_3'$), 6.12 (br s, 2H, H-4,4′), 6.73 (br s, 2H, H-3,3′), 7.03 (dd, 1H, $J$=8.1, 1.5, H-5″), 7.18 (d, 1H, $J$=8.1, H-6″), 7.23 (d, 1H, $J$=1.5, H-3″); $^{13}$C NMR $\delta$ ($CDCl_3$, 75.4 MHz): 13.66 ($CH_3$, $CH_3'$), 20.60 ($CH_3$), 108.11 (C-4,4′), 111.82 (C-3,3′), 123.28 (C-6″), 127.37 (C-2″), 127.84 (C-5″), 128.35 (C-2,2′), 130.13 (C-3″), 134.47 (C-4″), 138.56 (br, O–C═C–O), 138.75 (C-1″), 149.63 (C═N–), 154.10 (C-5,5′); MS $m/z$ (%): 369 ($M^+$, 4), 174 (81), 159 (100), 132 (79), 131 (44), 109 (74), 77 (48), 53 (57); IR (Nujol): 1738, 1669, 1494, 1466, 1270, 1214, 1118, 1103, 951, 790 cm$^{-1}$.

### 3.2.10. 2-(2,4-Dichlorophenylimino)-4,5-bis(5-methyl-2-furyl)-1,3-dioxole (**3j**)

Yield 74%; crystallization from petroleum ether gave pale yellow needles, mp 140 °C. (Found: C, 58.38; H, 3.43; N, 3.66. $C_{19}H_{13}Cl_2NO_4$ requires: C, 58.48; H, 3.36; N, 3.59); $^1$H NMR $\delta$ ($CDCl_3$, 300 MHz): 2.37 (s, 6H, $CH_3$, $CH_3'$), 6.12 (br s, 2H, H-4,4′), 6.74 (br s, 2H, H-3,3′), 7.18–7.24 (m, 2H, H-5″,6″), 7.41 (d, 1H, $J$=2.1, H-3″); $^{13}$C NMR $\delta$ ($CDCl_3$, 75.4 MHz): 13.65 ($CH_3$, $CH_3'$), 108.06 (C-4,4′), 111.97 (C-3,3′), 124.37 (C-6″), 127.31 (C-5″), 128.40 (br, C-2,2′), 128.55 (C-2″), 129.01 (C-4″), 129.44 (C-3″), 138.33 (br, O–C═C–O), 140.31 (C-1″), 150.02 (C═N–), 154.26 (C-5,5′); MS $m/z$ (%): 391 ($M^+$+2, 2), 389 ($M^+$, 11), 174 (80), 159 (100), 131 (34), 109 (44), 77 (23), 53 (42); IR (Nujol): 1723, 1659, 1478, 1465, 1377, 1271, 1197, 1095, 1021, 966, 784 cm$^{-1}$.

### 3.2.11. 2-(4-Bromophenylimino)-4,5-bis(5-methyl-2-furyl)-1,3-dioxole (**3k**)

Yield 67%; crystallization from acetonitrile gave pale yellow needles, mp 124–126 °C. (Found: C, 56.89; H, 3.48; N, 3.55. $C_{19}H_{14}BrNO_4$ requires: C, 57.02; H, 3.53; N, 3.50); $^1$H NMR $\delta$ ($CDCl_3$, 300 MHz): 2.37 (s, 6H, $CH_3$, $CH_3'$), 6.13 (d, 2H, $J$=3.2, H-4,4′), 6.73 (d, 2H, $J$=3.2, H-3,3′), 7.16 (d, 2H, $J$=8.7, H-2″), 7.43 (d, 2H, $J$=8.7, H-3″); $^{13}$C NMR $\delta$ ($CDCl_3$, 75.4 MHz): 13.65 ($CH_3$, $CH_3'$), 108.03 (C-4,4′), 111.77 (C-3,3′), 116.73 (C-4″), 125.03 (C-2″), [128.10, 128.21 (C-2,2′)], 131.81 (C-3″), [138.40, 138.61 (O–C═C–O)], 142.68 (C-1″), 149.31 (C═N–), 154.17 (C-5,5′), 166.38 (C═O); MS $m/z$ (%): 401 ($M^+$+2, 11), 399 ($M^+$, 11), 174 (93), 159 (100), 131 (32), 109 (32), 90 (17); IR (Nujol): 1729, 1666, 1486, 1458, 1272, 1196, 1105, 961, 833, 805, 689 cm$^{-1}$.

### 3.2.12. 2-(4-Chloro-2-methylphenylimino)-4,5-bis(5-methyl-2-furyl)-1,3-dioxole (**3l**)

Yield 70%; crystallization from acetonitrile gave pale brown granules, mp 116–118 °C. (Found: C, 65.00; H, 4.41; N, 3.86. $C_{20}H_{16}ClNO_4$ requires: C, 64.96; H, 4.36; N, 3.79); $^1$H NMR $\delta$ ($CDCl_3$, 300 MHz): 2.27 (s, 3H, $CH_3$), 2.37 (s, 6H, $CH_3$, $CH_3'$), 6.12 (d, 2H, $J$=2.4, H-4,4′), 6.72 (br s, 2H, H-3,3′), 7.12–7.17 (m, 3H, H-3″,5″,6″); $^{13}$C NMR $\delta$ ($CDCl_3$, 75.4 MHz): 13.63 ($CH_3$, $CH_3'$), 18.11 ($CH_3$), 108.01 (C-4,4′), 111.73 (C-3,3′), 123.04 (C-6″), 126.14 (C-5″), 128.20 (C-2,2′)*, 128.52 (C-4″)*, 130.04 (C-3″), 133.30 (C-2″), 138.60 (O–C═C–O), 141.36 (C-1″), 148.68 (C═N–), 154.11 (C-5,5′); MS $m/z$ (%): 369 ($M^+$, 4), 174 (90), 159 (100), 132 (28), 131 (39), 109 (68), 77 (45), 53 (52); IR (Nujol): 1723, 1663, 1485, 1463, 1274, 1221, 1111, 1024, 965, 793 cm$^{-1}$.

### 3.2.13. (E)-1,2-Di(2-furyl)vinylene bis(N-phenylchloroformimidate) (**4a**)

Yield 8%; crystallization from acetonitrile gave yellow prisms, mp 173–175 °C. (Found: C, 61.52; H, 3.38; N, 6.00. $C_{24}H_{16}Cl_2N_2O_4$ requires: C, 61.69; H, 3.45; N, 5.99); $^1$H NMR $\delta$ ($CDCl_3$, 200 MHz): 6.57 (dd, 2H, $J$=3.6, 1.9), 6.76 (dd, 4H, $J$=8.4, 1.4), 6.85 (dd, 2H, $J$=3.7, 0.6), 7.10 (tt, 2H, $J$=7.4, 2.0), 7.22–7.31 (m, 4H), 7.58 (dd, 2H, $J$=1.6, 0.7); $^{13}$C NMR $\delta$ ($CDCl_3$, 50.3 MHz): 111.62 (CH), 112.33 (CH), 121.25 (CH), 124.93 (CH), 128.89 (CH), 133.74 (C), 138.25 (C), 143.58 (CH), 144.64 (C), 145.60 (C); MS $m/z$ (%): 467 ($M^+$+1, 4), 431 (16), 313 (34), 312 (100); IR (Nujol): 1697, 1596, 1490, 1278, 1133, 1080, 1061, 1019, 901, 751, 691 cm$^{-1}$.

### 3.2.14. (E)-1,2-Di(2-furyl)vinylene bis[N-(4-chlorophenyl)-chloroformimidate] (**4b**)

Yield 12%; crystallization from acetonitrile gave pale brown needles, mp 211–213 °C. (Found: C, 53.71; H, 2.69; N, 5.17. $C_{24}H_{14}Cl_4N_2O_4$ requires: C, 53.76; H, 2.63; N, 5.22); $^1$H NMR $\delta$ ($CDCl_3$, 300 MHz): 6.56 (dd, 2H, $J$=3.3, 1.7), 6.68 (d, 4H, $J$=8.7), 6.81 (d, 2H, $J$=3.3), 7.22 (d, 4H, $J$=8.7), 7.57 (d, 2H, $J$=1.4); $^{13}$C NMR $\delta$ ($CDCl_3$, 75.4 MHz, +45 °C): 111.71 (CH), 112.35 (CH), 122.69 (CH), 129.08 (CH), 130.58 (C), 133.82 (C), 138.93 (C), 143.15 (C), 143.72 (CH), 145.56 (C); MS $m/z$ (%): 534 ($M^+$, 1), 174 (62), 172 (80), 111 (100), 95 (40), 75 (38); IR (Nujol): 1693, 1486, 1379, 1285, 1135, 1087, 903, 836, 751 cm$^{-1}$.

### 3.2.15. (E)-1,2-Di(2-furyl)vinylene bis[N-(2,4-dichlorophenyl)-chloroformimidate] (**4c**)

Yield 11%; crystallization from acetonitrile gave pale green needles, mp 193–195 °C. (Found: C, 47.76; H, 1.95; N, 4.61. $C_{24}H_{12}Cl_6N_2O_4$ requires: C, 47.64; H, 2.00; N, 4.63); $^1$H NMR $\delta$ ($CDCl_3$, 200 MHz): 6.58 (dd, 2H, $J$=3.4, 1.3), 6.68 (d, 2H, $J$=8.5), 6.86 (d, 2H, $J$=3.5), 7.15 (dd, 2H, $J$=8.5, 2.1), 7.33 (d, 2H, $J$=2.1), 7.57–7.59 (m, 2H); $^{13}$C NMR $\delta$ ($CDCl_3$, 50.3 MHz): 112.02 (CH), 112.32 (CH), 123.07 (CH), 126.86 (C), 127.51 (CH), 129.72 (CH), 133.96 (C), 141.20 (C), 141.35 (C), 143.94 (CH), 145.36 (C); MS $m/z$ (%): 602 ($M^+$, 2), 380 (26), 208 (98), 206 (100), 193 (19), 171 (24), 147 (25), 145 (41), 95 (61); IR (Nujol): 1691, 1474, 1377, 1288, 1166, 1149, 1099, 911, 736 cm$^{-1}$.

### 3.2.16. (E)-1,2-Di(2-furyl)vinylene bis[N-(4-cyanophenyl)-chloroformimidate] (**4d**)

Yield 11%; crystallization from acetonitrile gave yellow flakes, mp 225–227 °C. (Found: C, 60.49; H, 2.70; N, 10.78. $C_{26}H_{14}Cl_2N_4O_4$ requires: C, 60.36; H, 2.73; N, 10.83); $^1$H NMR $\delta$ (DMSO-$d_6$,

200 MHz): 6.82 (br s, 2H), 6.94 (d, 4H, $J$=8.2), 7.02 (d, 2H, $J$=3.2), 7.85 (d, 4H, $J$=8.2), 8.06 (s, 2H); $^{13}$C NMR $\delta$ (DMSO-$d_6$, 50.3 MHz): 107.80 (C), 112.45 (CH), 112.84 (CH), 118.57 (C), 121.84 (CH), 132.58 (CH), 133.73 (C), 139.97 (C), 144.05 (CH), 145.57 (C), 148.00 (C); MS $m/z$ (%): 516 ($M^+$, 0.1), 165 (32), 163 (100), 147 (12), 144 (14), 102 (70), 95 (40), 75 (10); IR (Nujol): 3129, 2227, 1694, 1601, 1501, 1486, 1281, 1134, 1086, 1028, 912, 845, 759 cm$^{-1}$.

*3.2.17. (E)-1,2-Di(2-furyl)vinylene bis[N-(4-bromophenyl)-chloroformimidate] (**4e**)*

Yield 13%; crystallization from acetonitrile gave pale brown needles, mp 238–240 °C. (Found: C, 46.14; H, 2.32; N, 4.50. $C_{24}H_{14}Br_2Cl_2N_2O_4$ requires: C, 46.11; H, 2.26; N, 4.48); $^1$H NMR $\delta$ ($CDCl_3$, 300 MHz, +55 °C): 6.55–6.61 (m, 2H), 6.62 (d, 4H, $J$=8.2), 6.80 (d, 2H, $J$=3.6), 7.37 (d, 4H, $J$=8.4), 7.56 (br s, 2H); $^{13}$C NMR $\delta$ ($CDCl_3$, 75.4 MHz, +55 °C): 111.65 (CH), 112.33 (CH), 118.22 (C), 123.00 (CH), 131.98 (CH), 133.81 (C), 138.78 (C), 143.66 (CH), 143.77 (C), 145.54 (C); MS $m/z$ (%): 622 ($M^+$, 1), 218 (61), 216 (44), 157 (53), 155 (58), 118 (28), 102 (85), 95 (100), 90 (45), 76 (77), 75 (59); IR (Nujol): 1699, 1484, 1284, 1134, 1088, 1010, 905, 829, 750 cm$^{-1}$.

*3.2.18. (E)-1,2-Di(2-furyl)vinylene bis[N-(2-chloro-4-methylphenyl)chloroformimidate] (**4f**)*

Yield 10%; crystallization from acetonitrile gave yellow needles, mp 174–176 °C. (Found: C, 55.41; H, 3.19; N, 5.07. $C_{26}H_{18}Cl_4N_2O_4$ requires: C, 55.34; H, 3.22; N, 4.96); $^1$H NMR $\delta$ ($CDCl_3$, 200 MHz): 2.26 (s, 6H), 6.56 (dd, 2H, $J$=3.5, 1.8), 6.63 (d, 2H, $J$=7.9), 6.88 (d, 2H, $J$=3.5), 6.95 (dd, 2H, $J$=8.1, 1.3), 7.13 (br s, 2H), 7.57 (d, 2H, $J$=1.7); $^{13}$C NMR $\delta$ ($CDCl_3$, 50.3 MHz): 20.73 ($CH_3$), 111.86 (CH), 112.27 (CH), 121.94 (CH), 125.43 (C), 127.88 (CH), 130.18 (CH), 133.78 (C), 135.78 (C), 139.81 (C), 140.53 (C), 143.76 (CH), 145.35 (C); MS $m/z$ (%): 562 ($M^+$, 1), 362 (27), 360 (41), 188 (64), 186 (100), 125 (37); IR (Nujol): 1687, 1494, 1462, 1379, 1162, 1136, 1087, 918, 855, 826, 744 cm$^{-1}$.

### 3.3. X-ray structure determination of compound 4f

*Crystal data*: $C_{26}H_{18}Cl_4N_2O_4$, $M_r$=564.22, monoclinic, space group $C2/c$, $a$=12.443(3), $b$=16.827(4), $c$=12.381(3) Å, $\beta$=99.966(18)°, $U$=2553.3(11) Å$^3$ at −100 °C; $Z$=4, $D_x$=1.468 g/cm$^3$, $F(000)$=1152, $\mu$=0.5 mm. *Data collection*: A pale yellow tablet 0.7×0.3×0.1 mm was mounted in inert oil on a glass fibre and transferred to the cold gas stream of the diffractometer (Siemens P4). Measurements were performed to $2\theta_{max}$ 50° with monochromated Mo K$\alpha$ radiation. Of 3469 measured reflections, 2262 were unique ($R_{int}$=0.021) and were used for all calculations. *Structure refinement*: The structures were refined anisotropically against $F^2$ (program SHELXL-97, G.M. Sheldrick, University of Göttingen). The methyl group was refined as a rigid group, other H with a riding model. After initial refinement, a significant peak of ca. 1.5 e/Å$^3$ was identified as an alternative position for C5, and the second disorder component was extended using an alternative position for the furyl group. The relative occupations of the disorder components refined to 3:1. Attempts to refine the structure in the alternative space group $Cc$ also led to a disordered structure. Because of the inherent problems associated with disordered structures, the molecular dimensions (especially of the disordered groups) should be interpreted with caution. The final $wR_2$ value was 0.0964 for all reflections, 189 parameters and 179 restraints (to the geometry of disordered groups), with $R_1$ 0.0391 for reflections with $I>2\sigma(I)$; max. $\Delta\rho$ 0.22 e/Å$^3$, $S$ 1.05.

Complete crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre under the number CCDC 669292.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## Supplementary data

X-ray structural data of compound **4f**; optimized geometries and energies of the ground state and the TS of **3a** are provided. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.02.082.

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32. The electrolyses can also be carried out in acetonitrile–sodium tetrafluoroborate.