

The Dimerization of 2,5-Diaryl-1,4-dithiin Radical Cations

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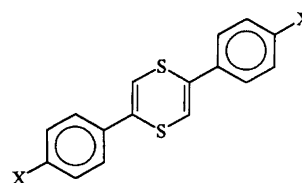
The electrochemical oxidation of five 2,5-diaryl-1,4-dithiins with aryl = *p*-anisyl (BAD), *p*-tolyl (BTD), phenyl (DPD), *p*-chlorophenyl (BCD) and *p*-nitrophenyl (BND) has been studied in MeCN–CH₂Cl₂ (1:1) by cyclic voltammetry (CV), derivative cyclic voltammetry (DCV) and linear sweep voltammetry (LSV) as well as constant current coulometry and product analyses. All compounds were found to undergo two quasi-reversible one-electron transfers to the radical cations and the dicationic species. The formal potential of the first redox couple and the life-time of the radical cation were found to decrease when the aryl group became more electron donating. The radical cation of BND was non-reactive on the timescale of slow-scan CV, whereas the radical cation of BAD was so reactive that it was impossible to outrun the follow-up reaction even at a scan rate of 1000 V s⁻¹. The number of electrons determined in the presence of 2,6-lutidine, added to prevent acid-catalyzed conversion of substrate, was between 1.1 and 1.5 except for BND, the radical cation of which catalyzed the oxidation of some unknown species in the solution. The major products from preparative electrolysis were the corresponding 2,2'-dimers, which were isolated in yields up to 20%. A detailed mechanistic and kinetic analysis of the dimerization, in the presence of 2,6-lutidine, involving the simultaneous fitting of theoretical data and experimental data obtained by LSV and DCV on a timescale covering several orders of magnitude, demonstrated that the process was of the radical cation–radical cation type and allowed for the determination of rate and equilibrium constants, k_1 and K_1 . In addition, the values of the heterogeneous electron transfer rate constant, k_s , and the transfer coefficient, α , could be determined this way. The values of k_1 were found to vary between $2.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ (BAD) and $8.7 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ (BCD). The Hammett-plot, $\log k_1$ vs. σ^+ , was linear indicating the importance of resonance stabilization for the dicationic transition state. The formal potentials for the reversible oxidation of the 2,2'-dimers to the radical cations were 70–120 mV higher than those for the monomers although AM1 calculations predicted the ionization potentials of the dimers to be slightly lower than those for monomers. It is suggested that differences in solvation more than counterbalance the purely electronic effects.

The formation and reactions of the radical cations of thianthrene (dibenzo-1,4-dithiin) and related compounds have been studied intensively and the results have been summarized in several reviews.^{1–4} However, with the exception of a number of ESR studies^{1,5–11} the radical cations derived from the parent ring system, 1,4-dithiin, and its derivatives have received much less attention and in particular, voltammetric studies are scarce.^{3,12–15}

As a part of our continuing interest in radical ion reactivity we reported recently on the electrochemical reduction of a series of 2,5-diaryl-1,4-dithiins in MeCN.¹⁶ The results of a detailed study of the electrochemical oxidation of the dithiins shown in Scheme 1 are now presented below. Parts of the experimental work required substrate concentrations too high to be obtained in MeCN and for that reason CH₂Cl₂ or 1:1 mixtures of MeCN and CH₂Cl₂ were used instead.

Results and discussion

Cyclic voltammetry (CV). In agreement with earlier work^{13,14} it was observed that the 2,5-diaryl-1,4-dithiins during CV in CH₂Cl₂ or MeCN–CH₂Cl₂ (1:1) at a voltage scan rate (v) of 0.1 V s⁻¹ gave rise to two oxidation peaks, O¹ and O². When the scan was reversed



X = OMe	(BAD)
X = Me	(BTD)
X = H	(DPD)
X = Cl	(BCD)
X = NO ₂	(BND)

Scheme 1.

between O^1 and O^2 , a reduction peak, R^1 , corresponding to O^1 was observed (except for BAD) as shown in Fig. 1 for a series of experiments in which nucleophilic and basic impurities were scavenged by addition of neutral alumina to the voltammetry solution.¹⁷ It is seen that the O^1/R^1 redox system appears reversible for BND, whereas a number of additional reduction peaks, R^i , R^{ii} and R^{iii} , associated with the reduction of products formed at O^1 were observed for the other compounds in the series when the scan was continued to potentials significantly lower than that of the O^1/R^1 system.

The values of $i_p/(C_{Dit}^\circ v^{1/2})$ for O^1 , where i_p is the peak current and C_{Dit}° the stoichiometric concentration of the dithiin, were independent of the height of R^1 and essentially the same for all compounds for $v > 0.5 \text{ V s}^{-1}$. In addition, the values of $i_p/(C_{Dit}^\circ v^{1/2})$ were close to that obtained for the one-electron oxidation of thianthrene to the radical cation, $i_p/(C_{Thi}^\circ v^{1/2})$, using the same working electrode, which demonstrates that the first oxidation peak for the dithiins is related to a one-electron process also.

Values of the peak potential, E_p^{ox} , and the formal potential, E° , for the first redox process are summarized in Table 1 and it is seen, not unexpectedly, that the more electron-donating the p -substituent, the lower the oxidation potential of the 2,5-diaryl-1,4-dithiin.

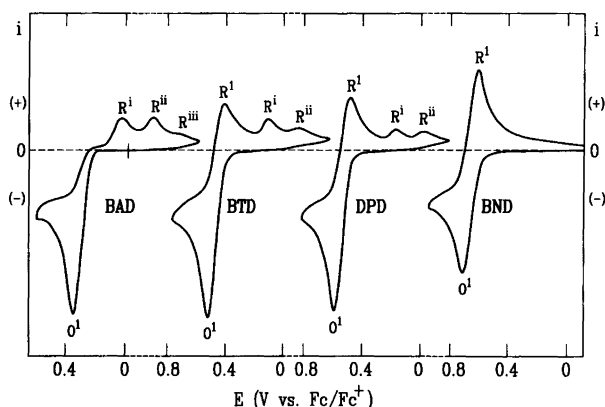


Fig. 1. Cyclic voltammograms for the oxidation of BAD, BTD, DPD and BND (2 mM) recorded at a Pt working electrode in CH_2Cl_2 , Bu_4NBF_4 (0.2 M) in the presence of neutral alumina; $v = 0.1 \text{ V s}^{-1}$; $T = 21^\circ\text{C}$.

The peak separations, $\Delta E_p = E_p^{ox} - E_p^{red}$, given in Table 1 for $v = 10 \text{ V s}^{-1}$, were found to be larger than that for an electrochemically reversible process, 59 mV,¹⁸ and to increase with increasing values of v indicating that the heterogeneous electron transfer process is quasi-reversible even at modest voltage scan rates.

The lifetime of the radical cations, as reflected by the magnitude of R^1 when the scan was reversed between O^1 and O^2 , depended strongly on the nature of the p -substituent as seen in Fig. 1. The BND radical cation was perfectly stable on the time scale of the experiment for v between 0.1 and 1000 V s^{-1} , whereas the BAD radical cation was so reactive that it was impossible to outrun the follow-up reaction even at $v = 1000 \text{ V s}^{-1}$. The results from studies of the effect of v on the magnitude of R^1 made it possible to set up the following order of reactivity for the radical cations: $\text{BAD} > \text{BTD} > \text{DPD} \approx \text{BCD} > \text{BND}$. Thus, in agreement with the earlier investigation¹⁴ we observe that the more difficult the dithiin is to oxidize, the less reactive is the resulting radical cation. We will return to this point later.

The origin of R^i , R^{ii} and R^{iii} will be discussed later also, but it can be concluded already at this stage that the products giving rise to these peaks are likely to be cations owing to their ease of reduction.

Reverse current corresponding to O^2 was not observed at $v = 0.1 \text{ V s}^{-1}$. However, when the scan rate was increased to 10 V s^{-1} two quasi-reversible redox couples were observed for three of the dithiins, BTD, DPD and BCP, and reverse current corresponding to O^2 for BND was clearly seen. This indicates that O^2 does indeed reflect the further oxidation of the radical cations to the dications.

Coulometry. The number of electrons, n , associated with the oxidation of the 2,5-diaryl-1,4-dithiins under the conditions of a preparative-scale experiment were determined by constant current coulometry.¹⁹ The results are summarized in Table 2 and it is seen that n -values close to one are observed for BTD, DPD and BCD.

A value less than one, 0.85, was observed for BAD. Cyclic voltammograms recorded with constant time intervals during the coulometry showed the accumulation of a product that was oxidized at a potential approximately

Table 1. Cyclic voltammetry data for the oxidation of 2,5-diaryl-1,4-dithiins.^a

Aryl group	Abbrev.	Peaks O^1/R^1			Peak O^2
		E_p^{ox}/V	E°/V^b	$\Delta E_p/\text{mV}^c$	E_p^{ox}/V
<i>p</i> -Anisyl	BAD	0.381	0.391 ^d	—	1.03 ^e
<i>p</i> -Tolyl	BTD	0.458	0.426	81.5	1.13
Phenyl	DPD	0.509	0.475	75.2	1.19
<i>p</i> -Chlorophenyl	BCD	0.568	0.534	73.7	1.24
<i>p</i> -Nitrophenyl	BND	0.700	0.668	80.3	1.31

^a Measured at a Pt working electrode in $\text{MeCN}-\text{CH}_2\text{Cl}_2$ (1:1), Bu_4NPF_6 (0.1 M) at $T = 20^\circ\text{C}$ and $v = 1 \text{ V s}^{-1}$ unless otherwise stated. The potentials are given versus the ferrocene/ferrocenium reference system. ^b Determined as $\frac{1}{2}(E_p^{ox} + E_p^{red})$. ^c $E_p^{ox} - E_p^{red}$ at $v = 10 \text{ V s}^{-1}$. ^d At $v = 100 \text{ V s}^{-1}$. ^e Approximate value due to the small magnitude of O^2 .

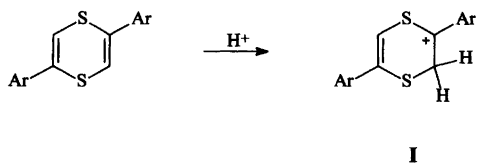
Table 2. Coulometric n -value for the oxidation of 2,5-diaryl-1,4-dithiins and the effect of addition of 2,6-lutidine.^a

		In the presence of 2,6-lutidine	
		8 mM	80 mM
BAD	0.85	0.95	—
BTD	0.97	1.13	1.14
DPD	1.04	1.22	1.46
BCD	0.93	1.17	1.38
BND	2.45	2.50 ^b	1.80 ^b

^a Determined by constant current coulometry in MeCN-CH₂Cl₂ (1:1), Bu₄NPF₆ (0.1 M) at $T=20^{\circ}\text{C}$. ^b Values corresponding to only partial conversion (see the text).

350 mV higher than that for BAD. The product peak was found to increase when 2,4-bis(*p*-anisyl)thiophene, isolated after preparative electrolysis (see below), was added to the solution at the end of the coulometry experiment. This partial conversion of BAD into 2,4-bis(*p*-anisyl)thiophene, a process that formally just involves the extrusion of a sulfur atom, appears to be caused by protons liberated during the oxidation. An independent NMR study showed that the acid-catalyzed conversion of BAD in non-aqueous solvents into 2,4-bis(*p*-anisyl)thiophene is indeed a feasible process involving as the first step the formation of **I** by protonation of the dithiin in the 3-position²⁰ (Scheme 2, Ar = *p*-anisyl). Thus, the low n -value observed for BAD is readily accounted for by this parallel, non-electrochemical consumption of substrate. The acid-catalyzed conversions of BTD, DPD and BCD are much slower processes²⁰ and did not interfere with the determinations of n .

As an attempt to suppress the side reaction a series of coulometry experiments were carried out in the presence of a base, 2,6-lutidine, which by virtue of the two methyl groups adjacent to the nitrogen atom would be expected to be only moderately nucleophilic towards the dithiin radical cations, but still to be a fast proton acceptor.^{21,22} As expected, n increased from 0.85 to a value close to one upon addition of 2,6-lutidine (8 mM), but at the same time the n -values determined for BTD, DPD and BCD increased to values slightly higher than one. At a 2,6-lutidine concentration of 80 mM the n -values for the three compounds were in the range 1.1–1.5. This indicates that a process with n higher than one competes more and more effectively with the one-electron process at increasing concentrations of 2,6-lutidine. Presumably this is an anodic substitution reaction ($n=2$) with 2,6-lutidine



Scheme 2.

acting as a nucleophile resulting in the formation of a 2,5-diaryl-1,4-dithiin carrying a 2,6-lutidinium substituent in the 3-position. In fact, an n -value close to 2 was observed for BCD when a non-hindered nucleophile, such as 4-methylpyridine, was used instead of 2,6-lutidine.

A new reduction peak at a potential approximately 2 V negative of O^I was observed in the cyclic voltammograms recorded during coulometry in the presence of 2,6-lutidine. The peak height increased linearly with electrolysis time and comparison of the E_p and $i_p/(C_{\text{Dit}}^{\circ}v^{1/2})$ values observed after 1 F with E_p and $i_p/(C_{\text{Lut}}^{\circ}v^{1/2})$ obtained for a solution containing 2,6-lutidine in the presence of a slight excess of acid left no doubt that protonated 2,6-lutidine or other 2,6-lutidinium ions (see below) were produced in an amount equivalent to that of the starting material during the oxidation of the dithiins.

The addition of 2,6-lutidine to the solution also caused the reduction peaks, Rⁱ, Rⁱⁱ and Rⁱⁱⁱ, to disappear showing that the cations assumed to be responsible for these peaks either are not formed or react with 2,6-lutidine.

The behavior of BND was quite different. The value of n was observed to be as high as 2.45, a value that was essentially unaffected by addition of 2,6-lutidine in low concentrations (8 mM). At higher concentrations n was observed to decrease to a value less than two, 1.80. Furthermore, the decay in substrate concentration with time was observed to be non-linear after approximately 25% of the substrate had been consumed and after approximately 50% the passage of charge caused no further conversion of BND. Thus, at this stage of the reaction the BND radical cation apparently acts as an electron transfer catalyst for the oxidation of some (unknown) species in the solution. Attempts to investigate this catalytic oxidation process further were not made. The n -values given in Table 2 refer to the stoichiometry observed early in the experiment where the decay in the substrate concentration was linear in time.

Preparative electrolyses. Oxidations on a preparative scale (1.5 mmol) were carried out in the presence of 2,6-lutidine (2.0 mmol) in a slight excess. The chloro derivative, BCD, was not included since, in all respects, it behaved similarly to DPD. The electrolyses were stopped after the passage of an amount of charge corresponding to 0.93–0.95 F. However, work-up of the electrolysis mixtures was difficult owing to the sensitivity to heat, light and moisture of some of the products and for this reason in particular the yields summarized in Table 3 were only modest. In addition, the electrolysis mixture might have contained small amounts of 2,6-lutidinium salts resulting from the anodic substitution reaction described above, but owing to the difficulty of separating ionic products from the supporting electrolyte such species were not identified or quantified. One product, the 2,2'-dimer, was isolated in yields ranging from 8% (DPD) to 22% (BAD). It was not possible to detect the

Table 3. Yields of products isolated after preparative electrolysis of 2,5-diaryl-1,4-dithiins.^a

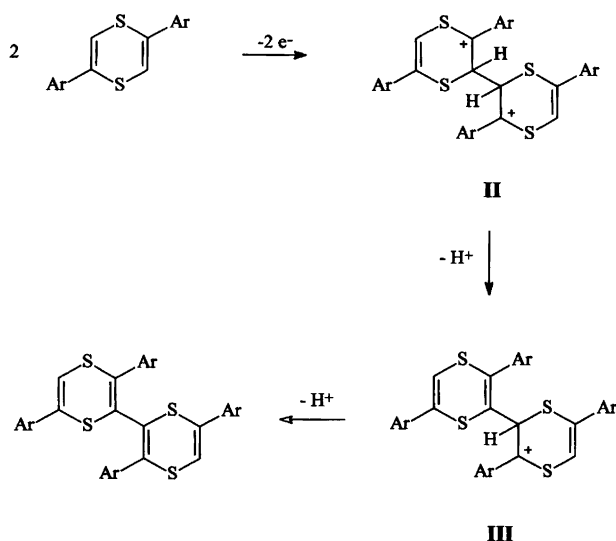
Substrate	Recovered substrate (%)	2,2'-Dimer (%)	Other products (%)
BAD	3	22	2,4-bis(<i>p</i> -anisyl)thiophene (5)
BTD	28	19	
DPD	30	8	
BND	65	—	2-formyl-2,4-bis(<i>p</i> -nitrophenyl)-1,3-dithiole (5)

^a In MeCN-CH₂Cl₂ (1:1), Bu₄NPF₆ (0.1 M) at *T* = 20 °C. Charge corresponding to 0.93–0.95 F was passed through the solution. The yields are based on the amount of dithiin subjected to electrolysis.

formation of a dimer from BND. Thus, the yields of dimer increase in the order BND (0%) < DPD < BTD < BAD, which is the same order as that observed by CV for the reactivity of the radical cations and thus it is tempting to suggest that the process with *n* = 1 observed during CV is indeed a dimerization reaction.

The small amounts of 2,4-bis(*p*-anisyl)thiophene isolated after oxidation of BAD, in spite of the presence of base, most likely resulted from slow thermal decomposition of BAD²³ during the electrolysis of remaining BAD during the work-up. The presence of 2-formyl-2,4-di(*p*-nitrophenyl)-1,3-dithiole in the reaction mixture from BND is possibly the result of a rearrangement of 2,5-di(*p*-nitrophenyl)-1,4-dithiin 1-oxide,²⁴ formed by the reaction of the BND radical cation with residual water. Polymeric products of unknown composition were formed in all cases as well.

Assignment of Rⁱ, Rⁱⁱ and Rⁱⁱⁱ. As mentioned above, the processes with *n* = 1 are likely to be dimerizations. Independent of the mechanism of the coupling step, which will be discussed in detail below, the first non-radical intermediate is **II**, which in the presence of a suitable base may lose two protons producing first **III** and then the 2,2'-dimer as shown in Scheme 3. When a suitable base is not present the most basic species are residual water and the starting material. Under these



Scheme 3.

conditions the protons are distributed among these two species and the 2,2'-dimer as protonated water and the three cations, **I** (protonated substrate), **II** (diprotonated dimer) and **III** (monoprotonated dimer), the relative amounts detected during CV being determined by the rate of proton transfer from **II** and **III** to water and substrate.

The assignment of Rⁱ, Rⁱⁱ and Rⁱⁱⁱ was based mainly on results obtained for BAD, the radical cation of which was not only the most reactive, but also resulted in the least reactive (acidic) cations and accordingly, the most intense reduction peaks (cf., Fig. 1). The relative intensities of Rⁱ, Rⁱⁱ and Rⁱⁱⁱ as observed at *v* = 0.1 V s⁻¹ under different reaction conditions are shown in Fig. 2.

The voltammogram obtained in CH₂Cl₂ at *T* = -15 °C (Fig. 2A) showed only the presence of Rⁱⁱ indicating that this peak is caused by reduction of the dimeric dication, **II**, the further reaction of which at this temperature is

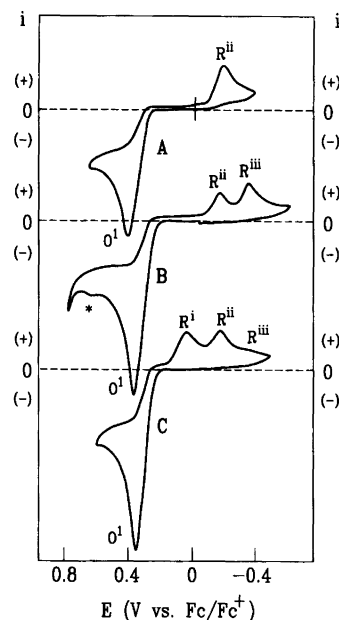


Fig. 2. Cyclic voltammograms for the oxidation of BAD (2 mM) recorded at a Pt working electrode at (A) *T* = -15 °C in purified CH₂Cl₂, (B) *T* = 21 °C in CH₂Cl₂ not purified before use and (C) *T* = 21 °C in purified CH₂Cl₂ in the presence of suspended neutral alumina. The supporting electrolyte was Bu₄NBF₄ (0.2 M); *v* = 0.1 V s⁻¹. The peak in (B) marked with an asterisk is caused by an impurity of 2,4-bis(*p*-anisyl)thiophene.

slow on the timescale of the experiment. This voltammetric pattern is similar to that observed in other cases where anodic oxidation of organic sulfur compounds leads to stable dimeric dication.^{25,26} When CV was carried out at room temperature using CH₂Cl₂ that had not been purified before use, both Rⁱⁱ and Rⁱⁱⁱ were seen on the reverse scan (Fig. 2B). This indicates proton transfer from **II** to basic impurities in solution resulting in the formation of **III** the reduction of which is seen as Rⁱⁱⁱ. Finally, when CV is carried out in the presence of suspended neutral alumina, protons are to some extent transferred to BAD resulting in the formation of **I**, the reduction of which is seen as Rⁱ (Fig. 2C). If, under these conditions, the scan rate is increased to 20 V s⁻¹ the height of Rⁱⁱ and Rⁱⁱⁱ grows relative to that of Rⁱ indicating that the timescale of the experiment is now comparable to that of the proton transfer from **II** and **III** to substrate.

The role of 2,6-lutidine. As already mentioned, it was initially expected that 2,6-lutidine would serve as a base for the protons liberated during the electrochemical oxidation, that is, by **II** and **III** on the way to the 2,2'-dimers (Scheme 3). However, much to our surprise further oxidation of the dimers to the radical cations, and possibly also to the dication, was not observed during CV. As reported below, the 2,2'-dimers are 70–120 mV more *difficult* to oxidize than the corresponding monomers and therefore, if formed, would result in a shoulder or a peak on the declining part of O¹. At least for BAD and BTD, for which the 2,2'-dimers were isolated in yields close to 20% after preparative electrolysis, it is inconceivable that the presence of 2,2'-dimers in these amounts would have escaped detection. Inspection of the voltammograms shown in Fig. 2B and C, for example, reveals not even a trace of additional current in the potential region right after O¹. We see only one possible explanation of this and that is that 2,6-lutidine reacts with **II** not as a base, but as a nucleophile resulting in the formation of adducts, possibly of type **IV** (Scheme 4). These would be expected not to be oxidized in the potential region close to O¹, but at the same time to form the 2,2'-dimers readily

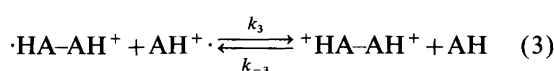
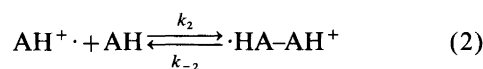
by elimination of 2,6-lutidinium ions during the work-up after preparative electrolysis. This behavior is in contrast with what has been observed during the anodic dimerization of, e.g., methoxy-arenes for which the formation of dimer dication of the type **II** is invariably followed by fast and irreversible deprotonation and, since the resulting dehydromimers in these cases are *easier* to oxidize than the monomers, subsequent oxidation of the dehydromimers to the radical cations in altogether 1.5 F processes.^{27–29} We realize that the suggestion that the reaction between **II** and 2,6-lutidine initially leads to the adduct, **IV**, instead of deprotonation to **III** and the 2,2'-dimer, is just a suggestion. Therefore, it is important to emphasize that this uncertainty concerning the primary products of the reaction between **II** and 2,6-lutidine has no implications for the kinetic analysis to follow, where only the rate of the reaction, but not the products, is of relevance.

Mechanisms and rate laws. Let us as a starting point consider the possible mechanisms for the reactions discussed above. An anodic coupling process is in general believed^{30,31} to proceed by a pathway involving as the first step the coupling of either two radical cations, eqn. (1), referred to below as **RR**, or of a radical cation and a molecule of substrate, eqn. (2), followed by the electron transfer step, (3), referred to as **RS**. In eqns. (1)–(3) and the equations to follow, AH represents the substrate (here the 2,5-diaryl-1,4-dithiin) and AH⁺ the corresponding radical cation.

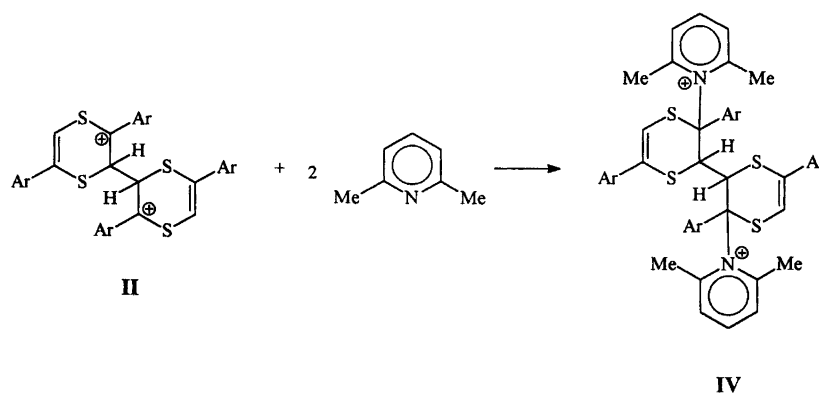
RR-coupling:



RS-coupling:

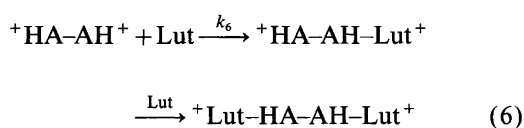
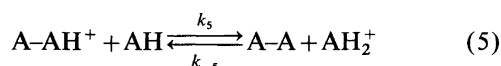
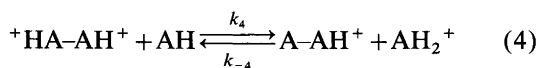


In either case the next steps are, in the absence of 2,6-lutidine, the (partial) deprotonation of ⁺HA-AH⁺

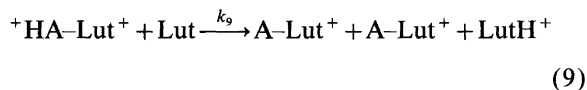
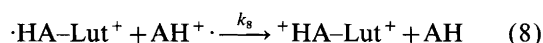
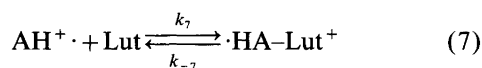


Scheme 4.

(II) to form A-AH⁺ (III) and A-A (the 2,2'-dimer) or, in the presence of 2,6-lutidine, the formation of ⁺Lut-HA-AH-Lut⁺ (IV). Thus, we have to consider the two proton transfer reactions, (4) and (5) and reaction (6). Since the acidities of AH₂⁺ (I), ⁺HA-AH⁺ (II) and A-AH⁺ (III) are expected to be similar it is unlikely that reactions (4) and (5) are strongly displaced to one side, whereas (6) is displaced to the right.



Finally, under conditions where 2,6-lutidine reacts as a nucleophile with AH⁺, we have eqns. (7)–(9), or a semblance of this scheme,³² with A-Lut⁺ representing a 2,5-diaryl-1,4-dithiin carrying a 2,6-lutidinium substituent.



Either of the coupling modes, **RR** or **RS**, may be combined with either of the two types of follow-up reaction and therefore we have to consider four different dimerization mechanisms: **RR**, (1), (4), (5) or (1), (6); **RS**, (2), (3), (4), (5) or (2), (3), (6); and the substitution mechanism (7)–(9).

Since an important aim of this work was to determine the mechanism and kinetics of the dimerization of 2,5-diaryl-1,4-dithiin radical cations the strategy for the work to follow was initially to find conditions, that is stoichiometric concentrations of the 2,5-diaryl-1,4-dithiin and 2,6-lutidine, under which the coupling reaction could be studied with little or no interference from the following steps (4)–(6) as well as the substitution reaction, (7)–(9). This obviously requires a concentration of 2,6-lutidine sufficiently high to eliminate the need for the dithiin to act as a base, but at the same time low enough that nucleophilic substitution is of only minor importance. It is obvious that a second-order coupling process, (1) or (2), also competes most favorably with the first-order substitution reaction (7), when the concentration ratio, $C_{\text{Dit}}^\circ/C_{\text{Lut}}^\circ$, is kept as high as possible. More insight into the competition between the various reaction pathways was obtained through a series of reaction order measurements using derivative cyclic voltammetry (DCV).³³

Reaction order measurements. Reaction order analysis by DCV was originally developed for systems for which the heterogeneous electron transfer is at equilibrium at the electrode surface, i.e., the Nernst equation applies. However, the results obtained by CV for the dithiins demonstrated that the heterogeneous electron transfer is quasi-reversible even at fairly low scan rates. Thus, in order to investigate whether the results obtained by DCV would be affected by contributions from heterogeneous kinetics, it was necessary first to estimate approximate values of the heterogeneous electron transfer rate constants, k_s .

Values of k_s may conveniently be obtained from a working curve, ΔE_p vs. $\log \Lambda_s$,³⁴ where $\Lambda_s = k_s[(RT)/(vnFD)]^{1/2}$, provided that the diffusion coefficient, D , is known. The value of D for DPD was determined from i_p recorded at $v=0.5 \text{ s}^{-1}$, where the influence of the heterogeneous electron transfer rate on the peak height is insignificant, and i_p for thianthrene ($D_{\text{Thi}} = 1.05 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ in MeCN at 20 °C³⁵) assuming that i_p is proportional to $D^{1/2}$, and accordingly $D_{\text{Dit}} = (i_p^{\text{Dit}}/i_p^{\text{Thi}})^2 D_{\text{Thi}}$,¹⁸ and assuming that diffusion coefficients in MeCN and MeCN-CH₂Cl₂ (1:1) are essentially the same. The resulting value of D_{DPD} at 20 °C was $0.8 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. It seems safe to assume also that D is only moderately dependent on the nature of the p -substituent and therefore that the value obtained for DPD may be applied for the whole series. The resulting values of k_s were in the range 0.1–0.3 cm s^{-1} . These are sufficiently large to allow a DCV reaction order analysis without taking k_s specifically into account, i.e., assuming Nernstian electron transfer, as long as high voltage scan rates are avoided. A more detailed discussion of this point follows later.

The reaction orders in substrate and the corresponding radical cation cannot be determined separately by DCV.³³ In fact, the DCV reaction order is made up of the *sum* of these two reaction orders and is defined by eqn. (10), in which v_x is the scan rate necessary to keep the derivative current peak ratio, $R_1' = -i_p'(\text{red})/i_p'(\text{ox})$, equal to x . The reaction order for 2,6-lutidine, R_{Lut} , is defined by eqn. (11).

$$R_{\text{Dit/Dit}^+} = 1 + \frac{\partial \log v_x}{\partial \log C_{\text{Dit}}^\circ} \quad (10)$$

$$R_{\text{Lut}} = \frac{\partial \log v_x}{\partial \log C_{\text{Lut}}^\circ} \quad (11)$$

The rate laws associated with the three reaction types, **RR**, **RS** and substitution, are summarized in Table 4 together with the DCV reaction orders as defined above. Only the so-called limiting cases have been included, that is reactions where all steps prior to the rate-determining step may be treated kinetically as equilibrium processes.

The results obtained experimentally for $R_{\text{Dit/Dit}^+}$ are summarized in Table 5. The values of x were chosen such that (too) high voltage scan rates were avoided. For the fast reaction of the BAD radical cation x was 0.35,

Table 4. Rate laws and DCV reaction orders for the reaction types **RR**, **RS** and substitution.

Reaction type ^a	RDS ^b	Rate law	$R_{\text{Dit/Dit}^{\cdot+}}$ ^c	R_{Lut} ^d
RR	(1)	$k_1[\text{AH}^{\cdot+}]^2$	2	0
RR	(4)	$\frac{k_1 k_4}{k_{-1}} [\text{AH}^{\cdot+}]^2 [\text{AH}]$	3	0
RR	(6)	$\frac{k_1 k_6}{k_{-1}} [\text{AH}^{\cdot+}]^2 [\text{Lut}]$	2	1
RS	(2)	$k_2 [\text{AH}^{\cdot+}] [\text{AH}]$	2	0
RS	(3)	$\frac{k_2 k_3}{k_{-2}} [\text{AH}^{\cdot+}]^2 [\text{AH}]$	3	0
RS	(4)	$\frac{k_2 k_3 k_4}{k_{-2} k_{-3}} [\text{AH}^{\cdot+}]^2 [\text{AH}]$	3	0
RS	(6)	$\frac{k_2 k_3 k_6}{k_{-2} k_{-3}} [\text{AH}^{\cdot+}]^2 [\text{Lut}]$	2	1
Subst.	(7)	$k_7 [\text{AH}^{\cdot+}] [\text{Lut}]$	1	1
Subst.	(8)	$\frac{k_7 k_8}{k_{-7}} [\text{AH}^{\cdot+}]^2 [\text{Lut}]$	2	1

^a **RR**: eqns. (1), (4), (5) or (1), (6); **RS**: eqns. (2), (3), (4), (5) or (2), (3), (6); Substitution: (7), (8), (9). ^b Rate-determining step. ^c Eqn. (10). ^d Eqn. (11).

Table 5. Values of the reaction order, $R_{\text{Dit/Dit}^{\cdot+}}$, obtained by DCV for the reaction of 2,5-diaryl-1,4-dithiin radical cations.^a

$C_{\text{Lut}}^{\circ}/\text{mM}$	BAD ^b	BTD ^c	DPD ^d	BCD ^d
0	—	2.33	2.53	2.57
43	2.02	2.18	1.93	1.94
160	—	—	1.36	—

^a Measured at a Pt working electrode in MeCN-CH₂Cl₂ (1:1), Bu₄NPF₆ (0.3 M); $T=20^{\circ}\text{C}$; the switch potential, $E_{\text{sw}}-E^{\circ}$, was 0.3 V. The substrate concentrations were in the range 0.4–6.0 mM. ^b Based on $v_{0.35}$ values. ^c Based on $v_{0.5}$ values. ^d Based on $v_{0.7}$ values.

corresponding to high conversion, whereas larger values, 0.5 or 0.7, corresponding to lower conversion, were used for the slower reactions observed for the BTD, DPD and BCD radical cations. It was seen that $R_{\text{Dit/Dit}^{\cdot+}}$ decreases with increasing C_{Lut}° from values higher than 2 in the absence of 2,6-lutidine to values close to 2 at $C_{\text{Lut}}^{\circ}=43$ mM. For a single compound, DPD, $R_{\text{Dit/Dit}^{\cdot+}}$ was also measured at $C_{\text{Lut}}^{\circ}=160$ mM resulting in a value, 1.36, significantly lower than 2. These results are in agreement with the following reaction schemes. In the absence of 2,6-lutidine, the reaction follows a dimerization mechanism in which the dithiin is forced to act partially as a base, e.g., **RR** or **RS** with the rate being partially controlled by reaction (4), which would result in $R_{\text{Dit/Dit}^{\cdot+}}$ larger than 2 since rate-determining reaction (4) would in the limit lead to $R_{\text{Dit/Dit}^{\cdot+}}=3$ (Table 4). Upon addition of 2,6-lutidine with $C_{\text{Lut}}^{\circ}=43$ mM the need for the dithiin as a base is eliminated and simple second-order dimerization mechanisms are followed, e.g.,

RR with rate-determining (1) or (6) or **RS** with rate-determining (2) or (6), all of which would result in $R_{\text{Dit/Dit}^{\cdot+}}=2$ (Table 4). Finally, at $C_{\text{Lut}}^{\circ}=160$ mM a significant part of the radical cation is apparently consumed in the substitution reaction with rate-determining (7), for which $R_{\text{Dit/Dit}^{\cdot+}}=1$, and thus an overall value of $R_{\text{Dit/Dit}^{\cdot+}}$ less than 2 is observed.

Results obtained for BAD and BTD with C_{Lut}° in the range 10–160 mM showed that R_{Lut} was close to zero independent of the concentration of substrate indicating that dimerization processes for these two rapidly reacting radical cations are best described as **RR** with rate determining (1) or **RS** with rate determining (2) or (3). Of these possibilities, reaction **RS** with rate-determining (3) can immediately be ruled out, since this mechanism would predict $R_{\text{Dit/Dit}^{\cdot+}}=3$ in disagreement with the observation that values significantly larger than 2 were observed only in the absence of 2,6-lutidine. The values of R_{Lut} obtained for DPD and BCD at a substrate concentration close to 1 mM are shown graphically in Fig. 3 and it is seen that R_{Lut} changes gradually from approximately 0.3 at $C_{\text{Lut}}^{\circ}\approx 10$ mM to values close to one at $C_{\text{Lut}}^{\circ}\approx 160$ mM. These data reflect that for the more slowly reacting radical cations the kinetics of the dimerization reactions at low substrate concentrations are partially determined by reaction (6), possibly with contributions from the substitution reaction as well. However, at higher substrate concentrations (4 mM) R_{Lut} was small for both substrates indicating that the second-order dimerizations, **RR** or **RS**, now compete favorably with the substitution reaction. At the same

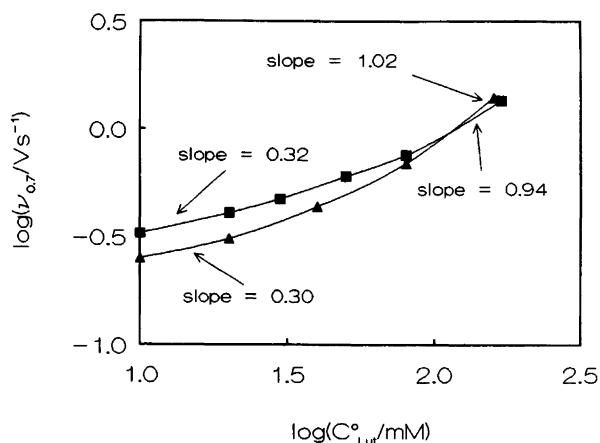


Fig. 3. The effect of the 2,6-lutidine concentration on the reaction rate for the radical cations of DPD (1.09 mM, ■) and BCD (0.97 mM, ▲) in MeCN-CH₂Cl₂ (1:1), Bu₄NPF₆ (0.1 M) at $T=20^{\circ}\text{C}$. The values of R_{Lut} given in the figure were determined as two-point slopes at $C_{\text{Lut}}^{\circ}=10$ –20 and 80–160 mM, respectively.

time the low reaction order in 2,6-lutidine tells us that reaction (6) is of only minor importance, that is the coupling processes are essentially irreversible in the applied scan rate range.

On the basis of these reaction order measurements it was concluded that the least interference from the reaction in which the substrate acts as a base, (4) and (5), and from the nucleophilic substitution reaction, (7)–(9), was obtained with an intermediate concentration of 2,6-lutidine, e.g., 43 mM, which resulted in a $R_{\text{Dit}/\text{Dit}^{\cdot+}}$ value close to 2 in all cases and substrate concentrations of 4 mM at which R_{Lut} was small only for DPD and BCD and essentially zero for BTD and BAD. Under these conditions, the mechanism discussion can be reduced to which of the coupling modes, **RR** or **RS**, are in operation, a question that cannot be answered on the basis of DCV reaction-order measurements, since both mechanisms would result in the same reaction order. Thus, a different experimental approach is necessary to distinguish between the two coupling modes.

One such approach would be to determine the half-peak width, $E_p - E_{p/2}$, by linear sweep voltammetry (LSV), since $E_p - E_{p/2}$ for the two mechanisms are predicted to differ considerably if studied under conditions where the reactions are under purely kinetic control.^{30,31} For these limiting cases $E_p - E_{p/2}$ takes the values 38.8 mV for **RR** with rate-determining (1) and 58.3 mV for **RS** with rate-determining (2) at $T=25^{\circ}\text{C}$.^{30,31} The experimental results obtained at different voltage scan rates are shown graphically in Fig. 4 as $E_p - E_{p/2}$ vs. $\log(C_{\text{Dit}}^{\circ}/\nu)$ for $C_{\text{Lut}}^{\circ}=43$ mM. First it is noticed that the rate of the heterogeneous electron transfer contributes, as expected, significantly in determining the half-peak width at high scan rates, at which all compounds gave rise to $E_p - E_{p/2}$ values far above that, 56 mV,¹⁸ for a reversible one-electron transfer reaction. However, at

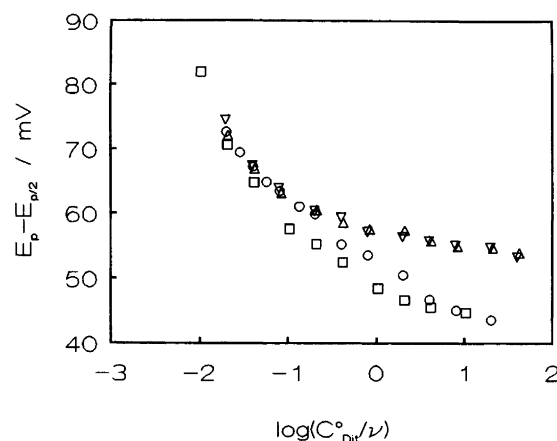


Fig. 4. Experimental values of $E_p - E_{p/2}$ for BAD (□), BTD (○), DPD (Δ) and BCD (▽) obtained at different voltage scan rates in MeCN-CH₂Cl₂ (1:1), Bu₄NPF₆ (0.3 M) in the presence of 2,6-lutidine (43 mM) at $T=20^{\circ}\text{C}$. $C_{\text{BAD}}^{\circ} \approx 2$ mM, $C_{\text{BTD}}^{\circ} \approx C_{\text{DPD}}^{\circ} \approx C_{\text{BCD}}^{\circ} \approx 4$ mM.

low scan rates, where the influence from the heterogeneous electron transfer kinetics is small, purely kinetic conditions are approached for the two fast reacting BAD and BTD radical cations and it is seen that the half-peak widths are clearly less than 50 mV, which rules out mechanism **RS**.

In conclusion, the mechanism of formation of the 2,2'-dimers appears to be most adequately described by mechanism **RR** with the coupling step (1) being rate-determining, although with small and variable contributions from reaction (6) and accordingly, back reaction (1).

The effect of quasi-reversible electron transfer on the LSV and DCV working curves and the determination of the rate constants. Since now the mechanism has been established it is possible to determine the rate constants, k_1 . However, as will become evident, the kinetic analysis may also provide values of k_s and the electrochemical transfer coefficient, α , as well as estimates of k_{-1} and k_6' ($=k_6[\text{Lut}]$) in the cases where reaction (6) is not sufficiently fast to prevent back reaction (1), that is re-dissociation of **II**. The reaction-order measurements (Table 5) indicated that the dimerizations in the presence of 2,6-lutidine (43 mM) proceed with the coupling step being essentially irreversible on the timescale used for obtaining the ν_x -values. Thus, it would seem natural to use these values, or even better, a series of measurements of R_1' recorded at different scan rates in the region close to ν_x , for the determination of k_1 . The latter involves the fitting of the experimental data to the appropriate DCV working curve, here R_1' vs. $\log \lambda_1$, where $\lambda_1 = k_1 C_{\text{Dit}}^{\circ} [RT/(nFv)]$. However, the preliminary CV results demonstrated that the heterogeneous electron transfer rate constants, k_s , for the 2,5-diaryl-1,4-dithiins were in the range 0.1–0.3 cm s⁻¹ and the results obtained for $E_p - E_{p/2}$ showed how this led to quasi-reversible behavior

at high voltage scan rates. Therefore, it is necessary to examine in more detail how the LSV and DCV working curves are affected by variations in k_s and α .

The results of a series of digital simulations³⁶ are shown in Fig. 5 as the effect of k_s on R_1' (A) and $E_p - E_{p/2}$ (B) for $\alpha=0.5$.

The theoretical data in Fig. 5A show that the influence of k_s on R_1' is small for $\lambda_1/\Lambda_s^2 < 0.1$ as long as R_1' is kept below 0.7 or for $\lambda_1/\Lambda_s^2 < 1$ at R_1' below 0.4. Keeping these restrictions in mind it is possible to determine k_1 for each of the dithiols by fitting the experimental data, plotted as R_1' vs. $\log(C_{\text{Dit}}/v)$, to the working curve. These fits should include experimental data obtained at scan rates giving values of R_1' not too far from 0.5 since scan rates much lower than that might result in data affected by the re-dissociation of II as discussed below. For reactions that are so fast that reliable values of R_1' cannot be obtained, e.g., the dimerization of BAD, working curves for $E_p - E^\circ$ (not shown)³⁷ may be used instead together with those for $E_p - E_{p/2}$.

With the values of k_1 now in hand it would seem possible to determine k_s also by fitting the experimental DCV data to the working curve in Fig. 5A now using data corresponding to $R_1' > 0.7$ where the effects of k_s are apparent, together with the data for $E_p - E_{p/2}$ (Fig. 4) and the working curves shown in Fig. 5B. However, both

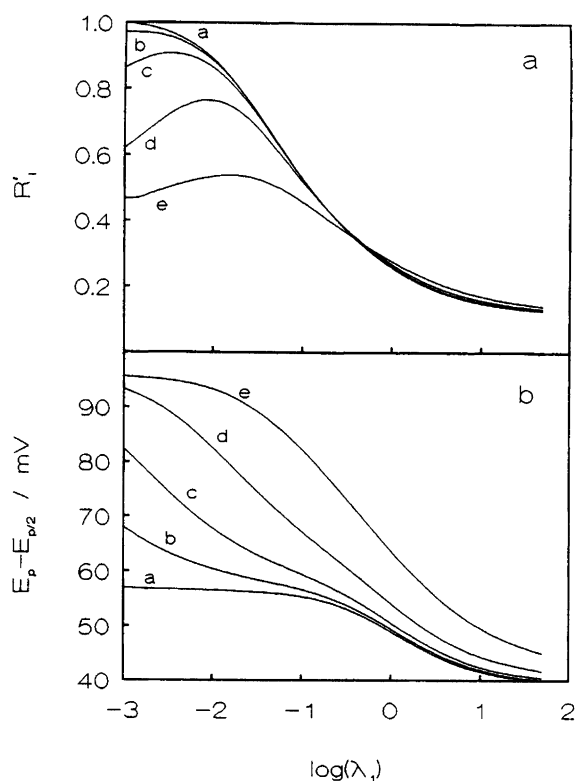


Fig. 5. Working curves showing the effect of k_s on R_1' (A) and $E_p - E_{p/2}$ (B) for irreversible dimerization at $\alpha=0.5$ and $\lambda_1/\Lambda_s^2=0.00001$ (a), 0.001 (b), 0.01 (c), 0.1 (d), 1.0 (e). The dimensionless parameters are given as $\Lambda_s = k_s[(RT)/(v\eta FD)]^{1/2}$ and $\lambda_1 = k_1 C_{\text{Dit}}^\circ [RT/(nFv)]$.

sets of working curves were simulated assuming $\alpha=0.5$ and it still remains to examine the influence of α on the working curves. The results of another series of digital simulations are shown in Fig. 6 as the effect of α on R_1' (A) and $E_p - E_{p/2}$ (B) for $\lambda_1/\Lambda_s^2=0.01$, and it is seen, as also found for the 'no reaction' case,³⁴ that even small deviations of α from 0.5 would be experimentally detectable. Thus, using these working curves it is possible to determine both k_s and α .

For the slowly reacting radical cations of BCD and DPD it was found, at low substrate concentrations, that the reaction order for 2,6-lutidine was slightly larger than zero indicating that reaction (6) does not completely suppress the re-dissociation of II. Contributions from these two reactions are therefore likely to be observed at low voltage scan rates, where, on the other hand, contributions from the heterogeneous electron transfer are expected to be small. A third series of simulations was carried out to investigate the effect of this partial reversibility of reaction (1) on the working curves. The results are shown in Fig. 7 as the effect of K_1 and k_{-1}/k_6' on R_1' (A) and $E_p - E_{p/2}$ (B) assuming Nernstian electron transfer.

The effect of reversibility of reaction (1) manifests itself as a minimum that moves up and to the left with decreasing values of the equilibrium constant (K_1) in a

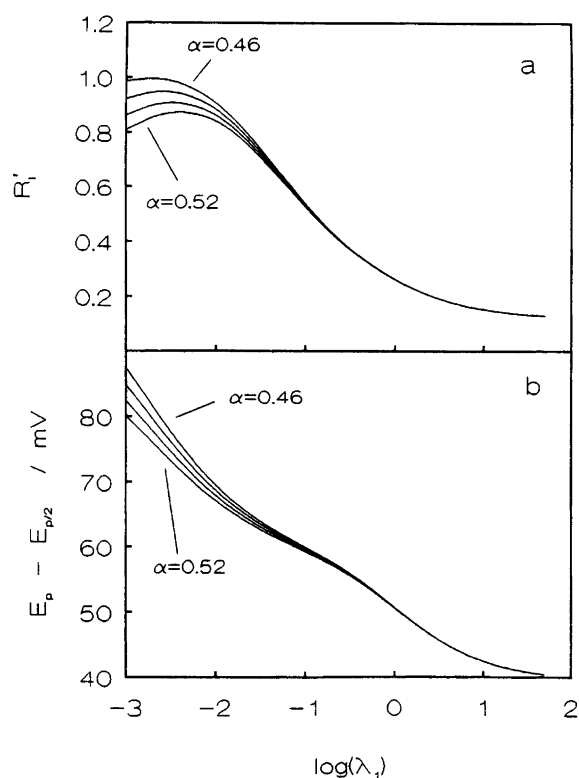


Fig. 6. Working curves showing the effect of α on R_1' (A) and $E_p - E_{p/2}$ (B) for irreversible dimerization at $\lambda_1/\Lambda_s^2=0.01$ and $\alpha=0.46$ (top), 0.48, 0.50 and 0.52 (bottom). The dimensionless parameters are given as $\Lambda_s = k_s[(RT)/(v\eta FD)]^{1/2}$ and $\lambda_1 = k_1 C_{\text{Dit}}^\circ [RT/(nFv)]$.

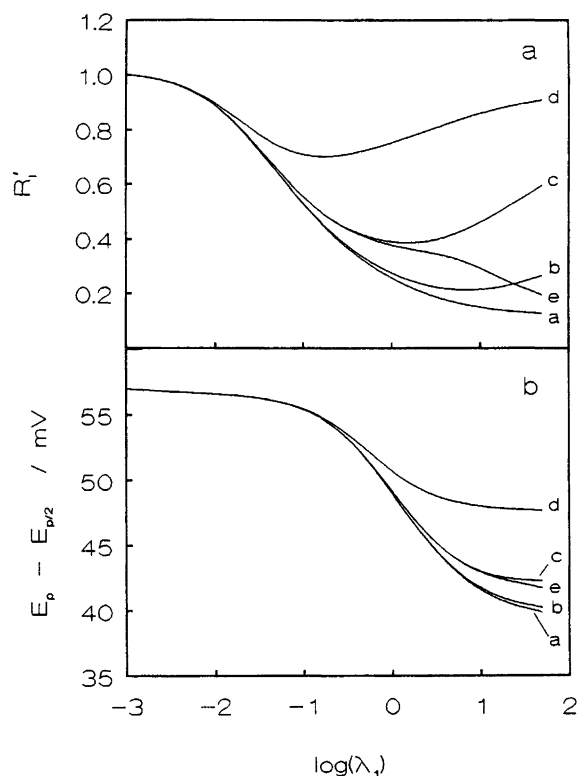


Fig. 7. Working curves showing the effect of K_1 and k_{-1}/k_6' on R_1' (A) and $E_p - E_{p/2}$ (B) assuming Nernstian electron transfer at $\lambda_{-1} = \lambda_6 = 0$ (a), $\lambda_1/\lambda_{-1} = 100$ and $\lambda_6 = 0$ (b), $\lambda_1/\lambda_{-1} = 10$ and $\lambda_6 = 0$ (c), $\lambda_1/\lambda_{-1} = 1$ and $\lambda_6 = 0$ (d) and $\lambda_1/\lambda_{-1} = 10$ and $\lambda_{-1}/\lambda_6 = 1$ (e). The dimensionless parameters are given as $\lambda_1 = k_1 C_{Dit}^\circ [RT/(nFv)]$, $\lambda_{-1} = k_{-1} [RT/(nFv)]$ and $\lambda_6 = k_6 C_{Dit}^\circ [RT/(nFv)]$.

fashion similar to what is observed for the working curves related to double potential step chronoamperometry^{38,39} as seen in Fig. 7A, curves a–d. At the same time decreasing K_1 results in a broadening of the LSV peak relative to that for an irreversible dimerization reaction as seen in Fig. 7B. The additional effect of reaction (6) is that the working curve for R_1' approaches that for irreversible dimerization (Fig. 7A, curve a) with increasing values of k_6 and/or decreasing scan rate. The difference between the curves c ($k_6' = 0$) and e ($k_{-1}/k_6' = 10$) serves to illustrate this point. A fit of the experimentally obtained R_1' -values and $E_p - E_{p/2}$ values obtained at low scan rates would therefore allow an estimate of k_{-1} (via K_1 and k_1) as well as an approximate value of k_6' from k_{-1}/k_6' and k_{-1} .

The experimental data obtained for a series of measurements for each of the four dithiins are shown in Fig. 8. These data, together with those already shown in Fig. 4 were analyzed in the manner just described and the resulting kinetic constants are summarized in Table 6.

Values of k_s for organic compounds are, as a rule, difficult to reproduce³⁴ and the 2,5-diaryl-1,4-dithiins are not exceptions in this respect. The origin of these difficulties is believed to be non-ideal electrode behavior, e.g., caused by electrode surfaces that are not smooth at

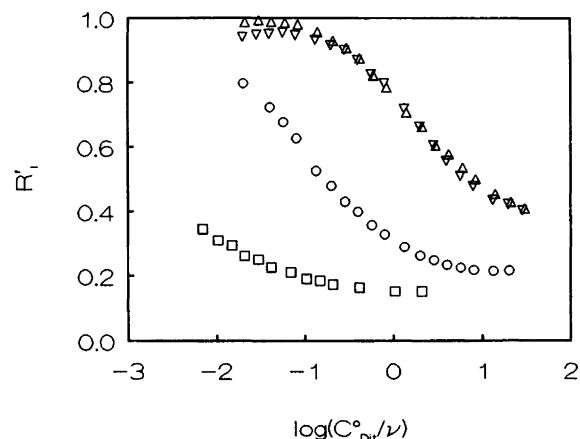


Fig. 8. Experimental values of R_1' obtained at different voltage scan rates for BAD (\square), BTD (\circ), DPD (\triangle) and BCD (∇). Same solutions as used for the data given in Fig. 4.

the microscopic level, and adsorption of substrate and/or electrode products. Also the amount of residual water in non-aqueous solvents, which is extremely difficult to control, may affect the kinetic data considerably. In order to minimize such effects the experimental data used for the determination of the kinetic parameters for each substrate were obtained using the same solution and working electrode. The resulting values of k_s were all within the range $0.1\text{--}0.3 \text{ cm s}^{-1}$ found during the preliminary work described above. In contrast, the values of α , were found to show only little day-to-day variation giving $\alpha = 0.50 \pm 0.02$ for all the substrates.

The advantage of determining several rate constants using only small fractions of the working curves has obviously to be paid for by a loss of precision (and accuracy). Therefore, a final control was made using the resulting values as input in simulations of working curves for each compound. These are shown in Figs. 9 and 10 together with the experimental data and it is seen that the agreement is in fact very good over the entire kinetic range. From the quality of the fit to the working curves it was concluded that the values of k_1 could be obtained with a precision of $\pm 15\%$, whereas the values of the equilibrium constants for formation of the dimer, K_1 , could only be obtained with a precision of $\pm 50\%$ owing to the lower sensitivity of the working curves towards changes in this parameter. Consequently, the k_{-1} values were determined only to a precision of approximately $\pm 60\%$. Determination of the ratio k_{-1}/k_6' was even less precise than the determination of K_1 , and the values of k_6' in Table 6 are therefore only valid within an order of magnitude.

From the data in Table 6 it is seen that the dimerization equilibrium constant, K_1 , varies by nearly three orders of magnitude on going from BAD ($1.4 \times 10^6 \text{ M}^{-1}$) to BCD ($2.5 \times 10^3 \text{ M}^{-1}$). Inspection of the values for k_1 and k_{-1} shows that this variation is caused almost exclusively by the strong dependence of k_1 on the nature

Table 6. Kinetic constants for the dimerization of dithiin radical cations.^a

Substrate	α	$k_s/\text{cm s}^{-1}$	$k_1/\text{M}^{-1} \text{s}^{-1}$	k_{-1}/s^{-1}	K_1/M^{-1}	$k_6'/\text{s}^{-1}{}^b$
BAD	0.50	0.10	2.2×10^6	1.5	1.4×10^6	—
BTD	0.50	0.18	2.9×10^4	1.2	2.5×10^4	<0.1
DPD	0.49	0.25	9.6×10^2	0.8	1.2×10^3	0.3
BCD	0.52	0.17	8.7×10^2	0.4	2.5×10^3	$<9 \times 10^{-3}$

^a In MeCN-CH₂Cl₂ (1:1), Bu₄NPF₆ (0.3 M) and C_{Lut}^o = 43 mM at T = 20 °C. ^b $k_6' = k_6 C_{\text{Lut}}^{\text{o}}$.

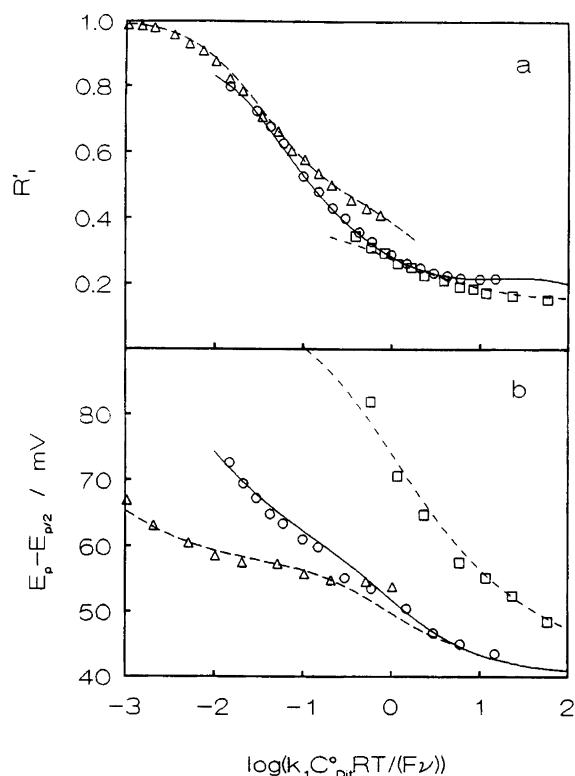


Fig. 9. The experimental data shown in Fig. 8 together with the working curves for R_1' (A) and $E_p - E_{p/2}$ (B). BAD (\square): $\lambda_1/\Lambda_s^2 = 4$, $\lambda_1/\lambda_{-1} = 3000$, $\lambda_{-1}/\lambda_6 = 0$, $\alpha = 0.5$ and $\log \lambda_1 = 0$ when $\log(C_{\text{BAD}}^{\text{o}}/v) = -1.75$ (---). BTD (\circ): $\lambda_1/\Lambda_s^2 = 0.03$, $\lambda_1/\lambda_{-1} = 100$, $\lambda_{-1}/\lambda_6 = 10$, $\alpha = 0.5$ and $\log \lambda_1 = 0$ when $\log(C_{\text{BTD}}^{\text{o}}/v) = 0.13$ (—). DPD (\triangle): $\lambda_1/\Lambda_s^2 = 0.0005$, $\lambda_1/\lambda_{-1} = 5$, $\lambda_{-1}/\lambda_6 = 3$, $\alpha = 0.49$ and $\log \lambda_1 = 0$ when $\log(C_{\text{DPD}}^{\text{o}}/v) = 1.61$ (---). (BCD has been omitted for clarity).

of the *p*-substituent in the aryl group; k_{-1} is only little affected by substitution.

Substituent effects. The results obtained by CV (Table 1) demonstrated that the more electron donating the *p*-substituent, the lower the oxidation potential of the 2,5-diaryl-1,4-dithiin. The corresponding Hammett plot, E^{o} vs. σ , is linear as shown in Fig. 11 with the slope of the correlation line equal to 0.26 V. The analogous Hammett plot for the dimerization rate constants, $\log k_1$ vs. σ , showed distinct curvature, whereas a plot of $\log k_1$ vs. σ^+ was found to be linear, as seen in Fig. 12, with the slope, ρ , of the correlation line equal to -4.0 ± 0.3 ($r = 0.994$). Extrapolation of the line to *p*-nitro results in the prediction that k_1 for BND should be close to 1 M^{-1}

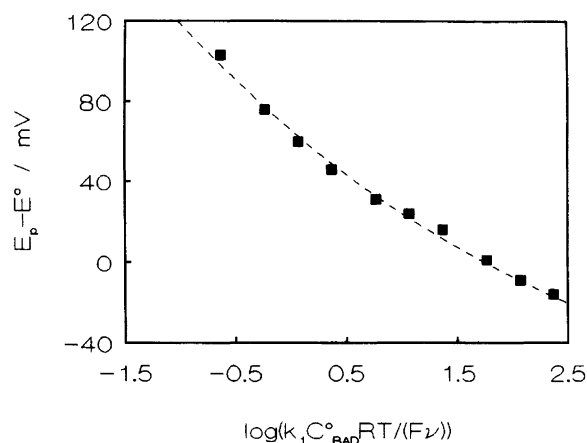


Fig. 10. Values of $E_p - E^{\text{o}}$ for BAD determined at different scan rates together with the working curves using the same parameters as given in the legend to Fig. 9.

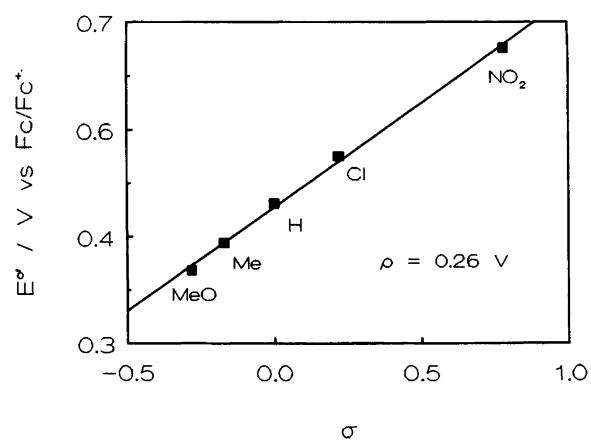


Fig. 11. Hammett plot, E^{o} vs. σ , for the oxidation of 2,5-diaryl-1,4-dithiins. The potentials are from Table 1.

s^{-1} . This would correspond to a $v_{0.7}$ value of approximately 3 mV s^{-1} at $C_{\text{Dit}}^{\text{o}} = 4 \text{ mM}$ in good agreement with the observation that the BND radical cation was observed to be non-reactive during CV even at $v = 0.1 \text{ V s}^{-1}$.

The observation of a linear relationship between $\log k_1$ and σ^+ , but not between $\log k_1$ and σ , indicates that resonance stabilization of the positive charge in the transition state plays an important role for the rate of the coupling reaction. In terms of classical resonance structures for the radical cations this can be illustrated for BAD as in Scheme 5. On the other hand, for the

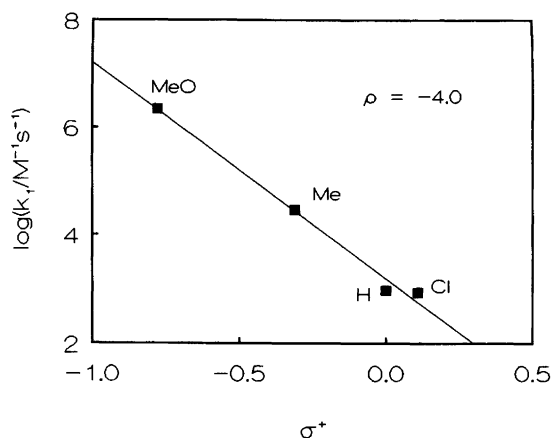
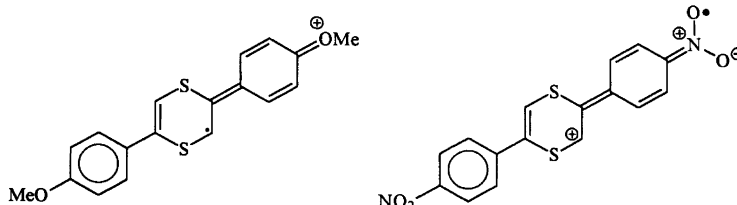


Fig. 12. Hammett plot, $\log(k_1/M^{-1} s^{-1})$, vs. σ^+ , for the dimerization of the 2,5-diaryl-1,4-dithiin radical cations. The rate constants are from Table 6.



Scheme 5.

BND radical cation an important resonance structure is without doubt one in which the unpaired electron is mainly located in the nitro group and the positive charge in the 3-position as also shown in Scheme 5. The effect of this is destabilization of the dicationic transition state to the extent that coupling is too slow to compete with other reactions, e.g., electron transfer or reactions with nucleophiles, and therefore is not observed. A similar difference in reactivity was observed for the reactions of the radical cations derived from 9-substituted anthracenes,⁴⁰ where dimerization was observed for the radical cations of 9-methoxy- and 9-phenyl-anthracene, whereas the radical cations of anthracene and 9-nitroanthracene were found instead to react predominantly with nucleophiles in solution.

Most other systematic studies of radical cation reactivity deal only with reactions between radical cations and nucleophiles.^{22,41,42} In these cases the plots of $\log k_{\text{nuc}}$ vs. σ^+ are linear with a positive slope, ρ . The results show also that the rate of the reaction increases with increasing $E^{\circ'}$ for the one-electron oxidation of the substrate, that is, the slope of a plot of $\log k_{\text{nuc}}$ vs. $E^{\circ'}$ is positive. This is in contrast with the negative slope implied by the Hammett plots in Figs. 11 and 12 for a plot of $\log k_1$ vs. $E^{\circ'}$ for the dimerization of the 2,5-diaryl-1,4-dithiin radical cations.

A similar set of relationships has been observed for the radical anions derived from a series of cinnamic acid esters.^{43,44} In aprotic solvents the radical anions were found to dimerize to the corresponding dimer dianions

resulting, after monoprotection and Dieckmann condensation, in high yields of the all-*trans*-3,4-diphenyl-2-methoxycarbonylcyclopentanones.⁴³ A plot of $\log k_{\text{dim}}$ vs. $E^{\circ'}$, was found to be linear with a positive slope, in contrast with the negative slope observed when $\log k_{\text{prot}}$ for protonation of the same radical anions by phenol was plotted against $E^{\circ'}$.⁴⁴ These parallel reactivity patterns for radical cations and radical anions are now under investigation.

Cyclic voltammetry of the 2,2'-dimers. The 2,2'-dimers could be oxidized reversibly to the radical cations during CV in MeCN-CH₂Cl₂ and, in addition, those derived from BTD and DPD gave rise to a second reversible one-electron couple at potentials approximately 240 mV higher than the first couple (Table 7) indicating significant electronic interaction between the dithiin units in the dimers. For comparison, the two consecutive one-electron

Table 7. Cyclic voltammetry data for the first and second one-electron oxidation of the 3,3',6,6'-tetraaryl-2,2'-bi(1,4-dithiins).^a

Aryl group	$E^{\circ'}(1)/V^b$	$E^{\circ'}(2)/V^b$	$\Delta E^{\circ'}(1)/V^c$
<i>p</i> -Anisyl	0.497	—	0.116
<i>p</i> -Tolyl	0.526	0.757	0.068
Phenyl	0.585	0.835	0.076

^a Measured at a Pt working electrode in MeCN-CH₂Cl₂ (1:1), Bu₄NPF₆ (0.1 M), at $T=25^\circ\text{C}$. The potentials are given relative to the ferrocene/ferrocenium reference system and are the averages of the potentials measured at $v=1$ and 10 V s^{-1} except for BAD where only $v=10 \text{ V s}^{-1}$ was used. ^b Determined as $\frac{1}{2}(E_p^{\text{ox}} + E_p^{\text{red}})$. ^c $E^{\circ'}(1) - E^{\circ'}$ (monomer); the data for the monomer are from Table 1.

oxidations observed for methoxy-substituted biphenyls are separated by 230–380 mV.⁴⁵

Comparison of the data for $E^{\circ'}$ for the substrate-radical cation redox couple with those for the oxidation of the corresponding monomers (Table 1) shows that the dimers are 70–120 mV more difficult to oxidize than the monomers. This is at odds with the data reported for most other monomer-dimer systems for which it is found that the dimers, owing to their more extended π -systems, are easier to oxidize than the monomers.^{27–29} More insight into the origin of this observation was gained through a series of semiempirical calculations (AM1) of the ionization potential (IP) for the DPD monomer and 2,2'-dimer. (See the Experimental section). The results

show that the calculated value of IP for the DPD dimer (8.10 eV) is indeed lower than that for the DPD monomer (8.27 eV) although the difference is only small. However, the observation that decreasing (calculated) values of IP are accompanied by increasing solution oxidation potentials is not unique and has also been observed for substituted hydrazines⁴⁶ and most likely reflects that the differences in solvation between the monomer and dimer systems more than counterbalance the purely electronic effects.

Experimental

Chemicals. The 2,5-diaryl-1,4-dithiins were prepared according to literature procedures.^{47,48} The supporting electrolyte, Bu₄NPF₆³⁴ or Bu₄NBF₄,⁴⁹ was added to either CH₂Cl₂ (reagent grade or Rathburn, HPLC grade) or a 1:1 mixture with MeCN (Rathburn, HPLC grade) and the resulting solution was passed through a column of neutral alumina (ICN, Super I) before the 2,5-diaryl-1,4-dithiin was added. The 2,6-lutidine (Fluka, *purum*) was distilled before use.

CV, DCV and LSV measurements. The electrochemical equipment and measurement procedures were the same as earlier described.⁴⁹ The platinum working electrodes (*d*=0.6 mm) were polished frequently on silicon carbide paper #4000, using a Struers DAP-V polishing machine.

Constant current coulometry. 2,5-Diaryl-1,4-dithiin (0.1 mmol) was dissolved in the solvent (50 ml) containing 0.1 M Bu₄NPF₆. Dissolved oxygen was removed by purging with nitrogen. The anode was a platinum gauze. The catholyte was separated from the anolyte by a 3–4 mm thick layer of neutral alumina and a sintered glass disk. After addition of 2,6-lutidine the solution was subjected to an oxidation current of 30 mA. The decay of substrate and the formation of 2,6-lutidinium ions with time was monitored by CV.

Preparative electrolysis. 2,5-Diaryl-1,4-dithiin (1.5 mmol) was dissolved in 50 ml MeCN–CH₂Cl₂ (1:1) containing Bu₄NPF₆ (0.1 M). Nitrogen was passed through the solution before and during the electrolysis. The anode was a platinum gauze. The cathodic chamber was separated from the solution by a layer of 3–4 mm neutral aluminium oxide and a sintered glass disk. The oxidation current was 50 mA. 2,6-Lutidine (2 mmol) was added in 50 µl portions during the electrolysis at a rate such that the solution at all times contained a slight excess of this reagent. After the passage of an amount of charge corresponding to 0.93–0.95 F the electrolysis was stopped and the solvent evaporated off. The solid residue was extracted with diethyl ether and/or tetrachloromethane. The combined extracts were concentrated to an oil or a solid and then chromatographed on silica gel. The eluent was benzene (BAD), CCl₄ (BTD and DPD) or CH₂Cl₂ (BND). The yields of isolated products are given in Table 3. The analytical data are given below.

3,3',6,6'-Tetra(p-anisyl)-2,2'-bi(1,4-dithiin). Elem. anal.: Calc. C: 66.02%, H: 4.76%, S: 19.59%. Found C: 65.82%, H: 4.62%, S: 19.70%. NMR (CDCl₃): δ 3.73 (s, 6 H), 3.83 (s, 6 H), 6.55 (s, 2 H), 6.58 (d, 4 H), 6.90–6.85 (m, 8 H), 7.60 (d, 4 H); MS: 590 (*M*⁺–2S), 295 $\frac{1}{2}$ (*M*⁺–2S). UV–VIS (CH₂Cl₂): λ_{max}=283 nm (ε=37400).

3,3',6,6'-Tetra(p-tolyl)-2,2'-bi(1,4-dithiin).⁵⁰ Yellow oil. MS: 526 (*M*⁺–2S), 263 $\frac{1}{2}$ (*M*⁺–2S); NMR (CDCl₃): δ 2.25 (s, 6 H), 2.37 (s, 6 H), 6.61 (s, 2 H), 6.83 (s, 8 H), 7.11–7.58 (m, 8 H).

3,3',6,6'-Tetraphenyl-2,2'-bi(1,4-dithiin). Yellow oil. MS: 470 (*M*⁺–2S); NMR (CDCl₃): δ 6.69 (s, 2 H), 6.83–7.72 (m, 20 H). UV–VIS (CH₂Cl₂): λ_{max}=257 and 312 nm.

2-Formyl-2,4-di(p-nitrophenyl)-1,3-dithiole. NMR (CDCl₃): δ 6.53 (s, 1 H), 7.51–7.77 (2 d, 4 H), 8.37–8.18 (2 d, 4 H), 9.59 (s, 1 H). MS: 345 (*M*⁺–CHO), 299 [*M*⁺–(CHO+NO₂)], 253 [*M*⁺–(CHO+2NO₂)].

AM1 calculations. The AM1 program was part of a MOPAC package (version 6.0) installed on a local CONVEX computer. The calculations were carried out with fixed dihedral angles of the two SCCS planes in the 1,4-dithiin ring.¹⁶ The dihedral angle used was that resulting from the force-field method (MMX) calculations included in PCMODEL (version 88.500 from Serena Software). For the unsubstituted 1,4-dithiin the dihedral angle calculated by MMX is close to 120° in good agreement with the angle of 137° found experimentally.^{51–53} Calculation of IP for the unsubstituted dimer was carried out using the same approach as for the monomers.

Digital simulation. The simulations were carried out using the implicit method described by Rudolph.³⁶ The programs were written in PASCAL and executed on 386SX or 486 personal computers. The parameter, β, which determines the degree of exponential expansion, was 0.75 in all cases and the dimensionless diffusion constant, *D*^{*}, was 10⁵. Steps of 2.5 mV were used throughout.

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