

# Electrochemical study of the $\pi^*$ probe dye 5-nitro-5'-dimethylamino-2,2'-bisthiophene

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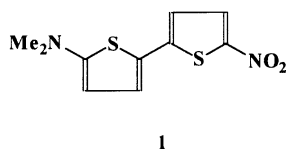
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**ABSTRACT:** Cyclic voltammograms of the solvatochromic dye 5-nitro-5'-dimethylamino-2,2'-bisthiophene (**1**), introduced recently as a sensitive  $\pi^*$  probe, were recorded in different solvents. An EPR spectrum of the anionic radical of **1** in DMSO was obtained and compared with other spectra of analogous substituted bisthiophene radicals. It was found that the presence of a donor–acceptor pair of substituents in  $\mathbf{1}^{\cdot-}$  reduces significantly the rotational barrier of the radical compared with the unsubstituted bithienyl radical anion  $\mathbf{2}^{\cdot-}$ . This is the result of an electronic repulsion between the donor ring fragment and the added electron in the coplanar radical, which does not exist in  $\mathbf{2}^{\cdot-}$ . © 1998 John Wiley & Sons, Ltd.

**KEYWORDS:** 5-nitro-5'-dimethylamino-2,2'-bisthiophene;  $\pi^*$  probe dye; cyclic voltammetry

## INTRODUCTION

Solvatochromic dyes have been extensively employed in the study of solute–solvent interactions and in the construction of various solvent polarity scales. One of these is the dipolarity–polarizability scale  $\pi^*$ , introduced by Kamlet and Taft's group two decades ago.<sup>1</sup> The original proposal of employing a set of seven solvatochromic probes for the construction of this scale proved cumbersome and was later superseded by the use of fewer, well chosen probes.<sup>2,3</sup> One of them was the 5-nitro-5'-dimethylamino-2,2'-bisthiophene (**1**), introduced by Effenberger and co-workers,<sup>4,5</sup> which offered the advantages of good solubility in all organic solvents and the clean, positive solvatochromism of its longest-wavelength charge-transfer band, in an otherwise transparent spectral region. Compound **1** has been utilized as an indicator of the medium dipolarity–polarizability of 35 pure solvents<sup>5</sup> and of 17 binary solvent mixtures of variable composition.<sup>6</sup>



In trying to gain a more complete understanding of the intramolecular charge-transfer processes which are

responsible for the solvatochromism of such dyes, physical chemists resort to theoretical tools, such as the calculation and properties of the electronic energy levels of these compounds. In addition, the experimental determination of redox potentials of these dyes may also shed some light on the role played by their donor and acceptor fragments in these charge-transfer processes. Thus, the  $E_T(30)$  dye, for example, was described as an 'internal battery,' made up of a phenoxide donor and pyridinium acceptor fragments.<sup>7</sup> Similar studies have been carried out with related dyes, such as pyridinium tetraphenylcyclopentadienide betaine,<sup>8</sup> with a description of the radical anions and cations generated by the corresponding one-electron dye reductions and oxidations.

In this work, we endeavoured to determine, by means of cyclic voltammetry, the oxidation and reduction potentials of dye **1** in different solvents, and to check whether the values obtained could be correlated with the  $\pi^*$  values of the solvents, which were derived from spectroscopic measurements. We coupled this investigation with the detection and characterization of the radical anion formed by electrochemical reduction of the dye in solution. In addition, we carried out semiempirical molecular orbital calculations on **1** and its radical anion, in order to interpret and rationalize the experimental results.

## EXPERIMENTAL

Cyclic voltammograms were recorded on a CV-27 BAS apparatus. The electron spin resonance spectrum of the

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radical anion derived from **1** was obtained with a Bruker ECS-106 instrument.

All solvents (Merck) were analytically pure and were further purified by standard procedures.<sup>9</sup> Dry ethanol was obtained by treatment of the commercial absolute solvent with calcium oxide, followed by distillation. The remaining solvents were distilled under atmospheric pressure (acetone and acetonitrile) or reduced pressure [formamide, dimethyl sulfoxide (DMSO) and dimethylformamide (DMF)] and stored over type 4A molecular sieves. Compound **1** was a gift from Professor F. Effenberger.

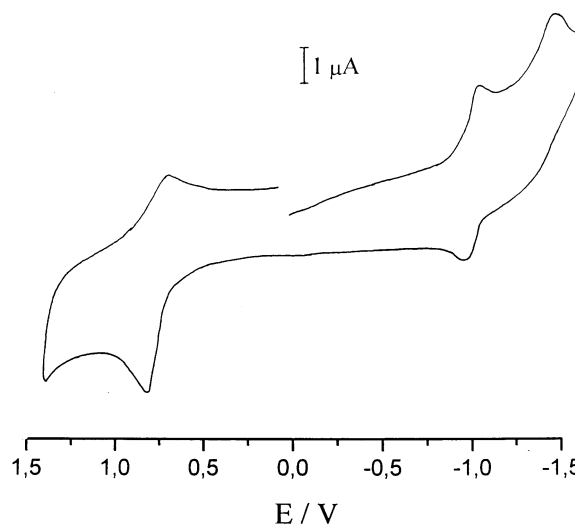
All cyclic voltammetry (CV) was carried out with a commercial glassy carbon working electrode, polished with alumina, using a saturated calomel solution as reference and a platinum wire as the auxiliary electrode. Tetraethylammonium perchlorate (Aldrich,  $c = 0.1 \text{ mol dm}^{-3}$ ) was employed as supporting electrolyte in solutions of **1** ( $c = 10^{-3} \text{ mol dm}^{-3}$ ). IR compensation was used in all measurements. The CV experiments were carried out at 25 °C, employing a sweep rate that varied from 30 to 350  $\text{mV s}^{-1}$ .

The radical anion of the bithienyl dye was generated under nitrogen by the *in situ* electrolytic reduction of the substrate in DMSO. DPPH ( $\alpha, \alpha'$ -diphenyl- $\beta$ -picrylhydrazyl radical) was employed as reference for spectrum calibration. Simulation of the EPR spectrum was achieved with a program from Rochester University (USA).

Semiempirical molecular orbital calculations were performed with the MOPAC 6.0 package for an IBM-PC microcomputer, utilizing the AM1 method.<sup>10</sup> Geometry optimizations were carried out with the keyword PRECISE, to ensure a more stringent criterion for convergence.

## RESULTS AND DISCUSSION

The electrochemical behaviour of **1** in cyclic voltammetry was studied in ethanol, acetone, acetonitrile, DMF, DMSO and formamide. The typical voltammogram in DMSO shown in Fig. 1 has an oxidation wave around 0.70 V, assigned to the formation of a radical cation, and a quasi-reversible one-electron reduction potential around  $-1.0 \text{ V}$ , corresponding to the formation of a radical anion of **1**. The anodic–cathodic peak separation for this quasi-reversible process increased slightly with the sweep rate, in a range which was dependent on the solvent: 0.04–0.06 mV in acetone, 0.07–0.12 mV in acetonitrile and 0.05–0.09 mV in DMSO and DMF. In the last two solvents, the reduction wave assumed a more reversible profile when the sweep was reversed before the irreversible cathodic peak. In addition, a third, irreversible reduction process around  $-1.31 \text{ V}$  was also observed. This corresponded to a further reduction of



**Figure 1.** Cyclic voltammogram of **1** ( $c = 10^{-3} \text{ mol dm}^{-3}$ ) in DMSO, utilizing tetraethylammonium perchlorate ( $0.1 \text{ mol dm}^{-3}$ ) as the supporting electrolyte. The sweep direction is clockwise, with a rate of  $200 \text{ mV s}^{-1}$ .

the nitro derivative to the corresponding hydroxylamine, a four-electron process characteristic of nitroarenes.<sup>11</sup>

The oxidation and reduction half-wave potentials of **1** are given in Table 1, together with the dipolarity–polarizability values  $\pi^*$  of all the solvents.

The search for possible correlations between the  $\pi^*$  values and the half-wave potentials of dye **1** was rendered difficult by the fact that all of the voltammograms obtained exhibited quasi-reversible and, sometimes, even irreversible processes. Thus, as can be seen from Fig. 1 the half-wave profiles obtained did not provide unambiguous values for the redox potentials of **1** in different media. This may be the reason for the poor correlations observed between the solvent  $\pi^*$  and the  $E_{\text{ox}}/E_{\text{red}}$  values in Table 1.

Using only the quasi-reversible values, the sensitivity of both  $E_{\text{ox}}$  and  $E_{\text{red}}$  to the solvent polarity was about the same, both potentials spanning a range of *ca* 80 mV. In addition, quasi-reversible  $E_{\text{ox}}/E_{\text{red}}$  values decreased with

**Table 1.** Variation of the half-wave oxidation ( $E_{\text{ox}}$ ) and reduction ( $E_{\text{red}}$ ) potentials of **1** in solvents with different dipolarity–polarizability values  $\pi^*$

Solvent	$\pi^*$ value <sup>a</sup>	$E_{\text{ox}}$ <sup>b</sup> (V)	$-E_{\text{red}}$ <sup>b</sup> (V)
Ethanol	0.57	0.80 <sup>c</sup>	1.08
Acetone	0.66	0.76	1.00
Acetonitrile	0.71	0.68	0.90
Dimethylformamide	0.87	0.69	0.94
Dimethyl sulfoxide	1.01	0.68	0.92
Formamide	1.14	0.80 <sup>c</sup>	0.62

<sup>a</sup> Ref. 6.

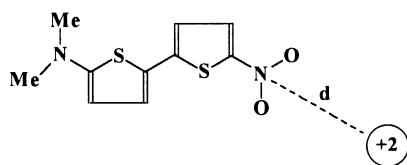
<sup>b</sup> Quasi-reversible processes, unless stated otherwise.

<sup>c</sup> Irreversible process.

the increased dipolarity–polarizability  $\pi^*$  of the medium. This last trend resulted from the fact that, in both processes, charged species were generated from a neutral molecule. As the solvent became more polar, solvation of the charged anion or cation relative to the neutral dye was increasingly facilitated, thus reducing the absolute potential of the corresponding process.

Although any trends from the potential values in Table 1 should be treated with caution, because of the limitations mentioned above, we decided to compare them with what could be expected from a theoretical approach, based on molecular orbital semiempirical calculations.

With this in view, we carried out calculations on the electronic levels of molecule **1** in media of different polarity. This was done by following a procedure employed before by us<sup>12,13</sup> and other workers<sup>14,15</sup> based on the perturbation induced on the geometry and energy levels of the solvatochromic dye by the proximity of a charge. The strength of the resulting electric field which acts upon the molecule may be modulated by simply varying the charge–dye distance. As a consequence, as we decrease this distance, we obtain structures and energy levels corresponding to the dye in increasingly ‘polar’ environments. For our analysis we considered three different situations: in the first, calculations were performed on the dye structure in the absence of any charge (structure **1**); in the second, a charge of +2 was positioned along the C–N axis of the Th–NO<sub>2</sub> fragment, at a distance of 6 Å from the nitrogen atom,



$$d = 6 \text{ \AA} \text{ (1a)}$$

$$d = 4 \text{ \AA} \text{ (1b)}$$

mimicking a medium of intermediate polarity (structure **1a**). Finally, by decreasing this distance to 4 Å, we obtained a highly polarized structure **1b**, corresponding

to a situation where the bithienyl dye is solvated by a polar solvent.

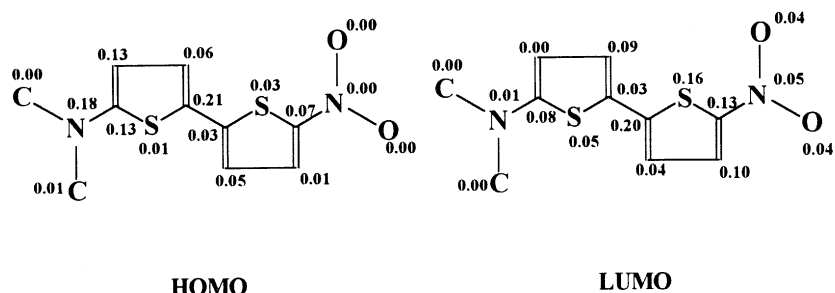
Before proceeding, we should be clear about the limitations of our model. The choice of the number and position of the charges when mimicking increasingly ‘polar’ environments is ultimately arbitrary. We therefore cannot relate any of the above structures with a particular solvent, but only say that the molecule polarization increases in the order **1** < **1a** < **1b**. This, however, is all we need for our analysis.

To a first approximation, we may equate the longest wavelength transition energy of the dye with the HOMO–LUMO energy gap,  $\Delta E$ . As can be seen from the charge distribution of the HOMO and the LUMO of structure **1**, shown in Fig. 2 this transition is accompanied by an overall charge transfer from the donor 5-dimethylaminothienyl fragment to the acceptor 5'-nitrothienyl moiety.

Table 2 gives the HOMO and LUMO energy levels and the  $\Delta E$  gap for structures **1**, **1a** and **1b**, calculated by the AM1 method. By inspection of the  $\Delta E$  value as the medium polarity is increased, we can see that positive solvatochromism (a decrease in  $\Delta E$  with increasing polarity) is expected for **1**, in agreement with experiment. We also notice that, of the two molecular orbitals, it is the LUMO which is affected mostly by the change in medium polarity. Thus, on going from **1** to **1b**, the energy of the LUMO varies from –1.48 to –6.02 eV (a variation of 4.54 eV), whereas the HOMO level shifts from –8.50 to –11.81 eV (a variation of 3.31 eV). The LUMO energy is associated with the one-electron gain by the molecule, whereas the oxidative loss of one electron should depend on the HOMO energy.

The above calculations would predict a slightly greater sensitivity of the oxidation potentials of **1** to the polarity variations of the medium. This trend might be recognized in Table 1 if the potential values for the irreversible processes are also taken into account. Otherwise, the agreement between the experimental data and the theoretical calculations is admittedly poor.

The formation of charged radical species from **1** was further investigated by electron paramagnetic resonance. Although we could not detect the radical cation formed by oxidation of the dye, the one-electron reduction of **1** in



**Figure 2.** Calculated HOMO and LUMO charge densities of dye **1**. Numbers refer to the squared coefficients of the p<sub>z</sub> atomic orbitals of all heavy atoms

**Table 2.** Calculated HOMO and LUMO energies and the HOMO–LUMO energy gap ( $\Delta E$ ) for the increasingly polarized structures **1**, **1a** and **1b**

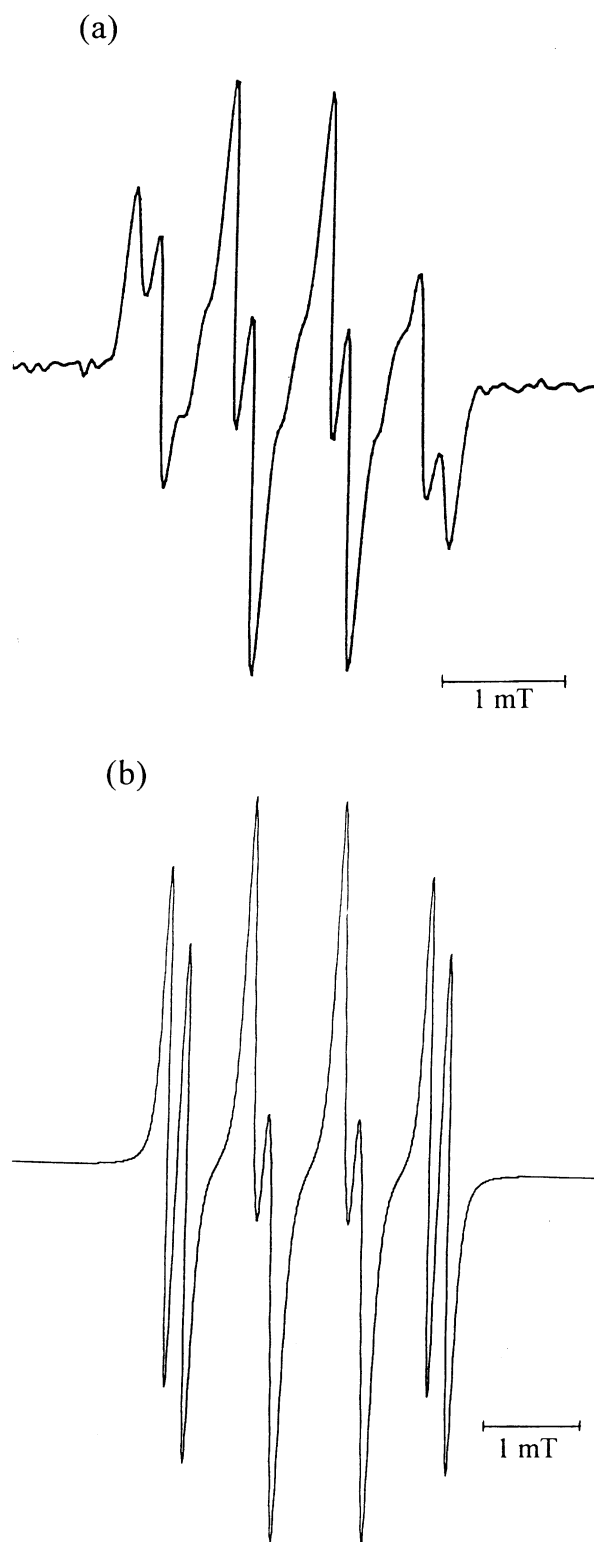
Structure <sup>a</sup>	HOMO energy (eV)	LUMO energy (eV)	Energy gap, $\Delta E$ (eV)
<b>1</b>	−8.50	−1.48	7.02
<b>1a</b>	−10.96	−4.85	6.11
<b>1b</b>	−11.81	−6.02	5.79

<sup>a</sup> Structures polarized by a charge of +2 in the vicinity of the dye, at a distance of 6 Å (structure **1a**) and 4 Å (structure **1b**) from the NO<sub>2</sub> group (see text).

DMSO yielded a radical anion which gave the EPR spectrum shown in Fig. 3(a).

A simulated spectrum is shown in Fig. 3(b), with a triplet assigned to a nitrogen atom and doublets corresponding to four different hydrogen atoms. The values of the hyperfine coupling constants obtained were  $a_N = 0.895$  mT,  $a_{H1} = 0.805$  mT,  $a_{H2} = 0.201$  mT,  $a_{H3} = 0.05$  mT and  $a_{H4} = 0.03$  mT. Comparison of the experimental with the simulated spectrum reveals some differences, consisting mainly in line broadening in the former, which is absent in the latter spectrum.

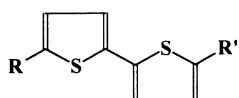
Evidence for equilibria between rotational isomers of bithienyl radicals has been provided by EPR studies of such systems.<sup>16,17</sup> The presence of two sets of lines in the EPR spectra of these radicals at room temperature was interpreted as arising from restricted rotation around the interannular bond. The rotational barrier for the *cis*–*trans* rotamer interconversion has been estimated by the INDO semiempirical method to be 26.8 kcal mol<sup>−1</sup> for the 2,2′-bithienyl radical anion.<sup>16</sup> Such a large barrier was found to be compatible with the fact that no exchange broadening could be observed in the EPR spectra of 5,5′-disubstituted-2,2′-bithienyl radicals even at temperatures as high as 100°C. An equilibrium between two rotational isomers might also account for the signal broadening observed in the spectrum of our bithienyl radical. This could explain the differences between our simulated spectrum, which refers to a single species, and the experimental lines, which arise from an equilibrium between two rotamers. The observed line broadening would then suggest that coalescence of the two spectra was already taking place at room temperature. Since this had not been observed for other bithienyl radicals, we had to conclude that our system had a much smaller rotational barrier than the systems reported by Pedulli *et al.*<sup>16</sup> This, however, was surprising. The high barrier found for those systems, much higher than the corresponding barrier of neutral 2,2′-bithienyl, was explained in terms of an increase in the double-bond character of the interannular link, as an electron was added to the LUMO of these molecules. In our case, with a donor–acceptor pair of substituents, charge transfer in the excited LUMO would enhance the double-bond character of this link even more, thus resulting in an even greater barrier to rotation.



**Figure 3.** (a) Experimental and (b) simulated EPR spectra of the radical anion of **1** in DMSO

In order to look for an explanation to accommodate both the reported observations and our results, we decided to employ semiempirical calculations to investigate in more detail the rotational isomerism of

disubstituted bithienyl radical anions. We therefore performed calculations with the AM1 hamiltonian on the radical anions derived from the bithienyl systems **1**, **2** and **3**.



$R = NMe_2$ ,  $R' = NO_2$  (**1**)

$R = R' = H$  (**2**)

$R = R' = CHO$  (**3**)

The unsubstituted bithienyl radical  $2^{\cdot-}$  decayed rapidly at temperatures higher than  $-40^\circ C$ <sup>16</sup>. Nevertheless, this system was taken in the present study as a reference structure for both  $1^{\cdot-}$  and  $3^{\cdot-}$ .

We utilized the AM1 method to optimize the geometries of the bithienyls **1**, **2** and **3** and of the corresponding anion radicals  $1^{\cdot-}$ ,  $2^{\cdot-}$  and  $3^{\cdot-}$ . In all cases we obtained the coplanar *trans* and *cis* conformations as the most stable rotamers, the former being slightly more stable than the latter ( $0.3\text{--}0.5\text{ kcal mol}^{-1}$ ) in the case of the radicals. We next estimated the rotational barrier for each of the radical anions, following the protocol described by Pedulli *et al.*<sup>16</sup> Thus, we fixed the geometry of the two ring systems and optimized the interannular bond distance  $C(2)\text{--}C(2')$  for a torsional angle of  $90^\circ$ . The rotational barrier was then assumed to be equal to the energy difference between the structure obtained and the stable *trans* conformation. These values are given in Table 3. They are in general smaller than the values obtained by Pedulli *et al.*, who employed the INDO method in their calculations. We should not be concerned with absolute values for our calculated rotational barriers. Besides all approximations inherent to our method, the results obtained should apply to the gas phase, and not to a substrate surrounded by solvating DMSO molecules. The trends obtained are, however, illuminating. Radical  $1^{\cdot-}$  should exhibit a much smaller barrier to rotation than radicals  $2^{\cdot-}$  and  $3^{\cdot-}$ , which should behave more or less similarly. Our experimental results agree with this. The EPR spectra of the two radical conformers from **1** coalesce at room temperature, whereas those from **3** do not show any line broadening even at  $100^\circ C$ . The

bithienyl radical anion  $2^{\cdot-}$  could not be studied above  $-40^\circ C$ , but the reported theoretical results predicted a similar behaviour to that of  $3^{\cdot-}$ .<sup>16</sup>

The question now arises as to the reason for such differences. In fact, as argued above, the double-bond character of the interannular link in the LUMO should be greatest for dye **1**, the only bithienyl to exhibit a donor–acceptor pair of substituents and intramolecular charge-transfer across the system. Consequently, restriction to rotation should be greater for radical  $1^{\cdot-}$  than for the others.

That this is not the case argues for another effect which, so to speak, undermines this strengthening of the interannular link in the LUMO of these systems. This opposite effect arises from the conjugation itself between the two rings, which brings about an electronic repulsion between the added electron and the electron-donating 2-[5-(dimethylamino)thienyl] moiety. This repulsion, which does not exist in systems  $2^{\cdot-}$  and  $3^{\cdot-}$ , destabilizes the coplanar conformations of radical  $1^{\cdot-}$ , thus reducing the rotational barrier of the latter species. In other words, loss of stability on going from a coplanar to an orthogonal conformation is much more substantial for radicals  $2^{\cdot-}$  and  $3^{\cdot-}$  than for  $1^{\cdot-}$ .

Evidence for this can be gathered from Table 3, where we compare the calculated interannular bond distances for the three bithienyls, both as neutral species and as radical anions. It is seen that, as expected, this distance is shortest for **1**, because of internal charge transfer. Addition of one electron to the LUMO of these systems has the effect of enhancing the double-bond character of this link for all bithienyl radicals. This enhancement, however, is greater for systems  $2^{\cdot-}$  and  $3^{\cdot-}$  where no resulting electronic repulsion intervenes, than for  $1^{\cdot-}$ .

Further experimental evidence for this repulsive effect in  $1^{\cdot-}$  is provided by the estimated values of its hyperfine constants, which should differ appreciably from those reported for the analogous 5,5'-dinitro-2,2'-bithienyl radical anion.<sup>16</sup>

Hyperfine coupling constants for the radical anion derived from 2-nitrothiophene have been reported as  $a_N = 0.937\text{ mT}$ ,  $a_H = 0.565\text{ mT}$  (H *ortho* to  $NO_2$ ),  $a_H = 0.123\text{ mT}$  (H *meta*) and  $a_H = 0.453\text{ mT}$  (H *para*).<sup>18</sup> These values are much larger than those reported for

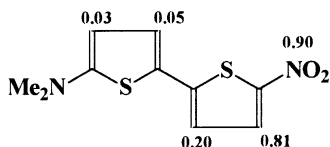
**Table 3.** Calculated parameters for bithienyls **1**, **2** and **3** and for their corresponding radical anions.

Parameter	System		
	<b>1</b>	<b>2</b>	<b>3</b>
Rotational barrier ( $\text{kcal mol}^{-1}$ )	4.8	12.4	14.7
$C(2)\text{--}C(2)$ bond distance in the neutral molecule ( $\text{\AA}$ )	1.422	1.424	1.425
$C(2)\text{--}C(2)$ bond distance in the radical anion ( $\text{\AA}$ )	1.395	1.386	1.387
$C(2)\text{--}C(2)$ bond shortening <sup>a</sup>	0.027	0.038	0.038

<sup>a</sup> On going from the neutral species to the radical anion.

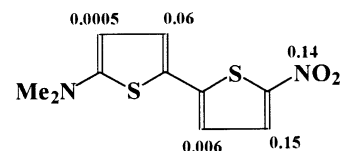
other radicals derived from symmetrical 5,5'-disubstituted bithienyl systems. Thus, for example, hyperfine constants for the 5,5'-dinitro-2,2'-bithienyl radical anion in DMSO were found to be  $a_N = 0.165$  mT,  $a_H = 0.134$  mT (H *ortho* to NO<sub>2</sub>) and  $a_H = 0.049$  mT (H *meta*).<sup>16</sup> These smaller values reflect the equal distribution of the single electron among the two thienyl rings, with the consequent decrease in spin densities on each ring. A similar effect is observed in the spectra of radical anions derived from nitroaromatics. The values of the hyperfine constants  $a_N$  and  $a_H$  corresponding to the nitrogen and the *ortho* hydrogen atoms of the nitrobenzene radical, 1.032 and 0.04 mT, respectively, are reduced to 0.17 and 0.01 mT, respectively, in the 1,4-dinitrobenzene radical anion<sup>19</sup>.

If we base ourselves on previously studied 5,5'-substituted-2,2'-bithienyl radicals, we may tentatively assign the estimated hyperfine constants for the *trans* rotamer of **1** as shown in the structure, where the spin densities are heavily concentrated on the nitrogen and the *ortho*-hydrogen atoms of the acceptor moiety of the molecule. Such large values of the  $a_N$  and  $a_H$  constants for the system **1**<sup>-</sup> are much closer to the values for the monothienyl radical from 2-nitrothiophene than to similar values for the 5,5'-dinitrobithienyl system. This is because the electronic repulsion that arises in the radical anion from replacing an electron-withdrawing NO<sub>2</sub> substituent at the 5'-position by the strong donor NMe<sub>2</sub> group has the effect of concentrating all the spin density of the added electron on the nitrothienyl moiety.



The spin densities which follow from the above assignment depart considerably from the theoretical LUMO densities calculated for **1** (Fig. 2). According to the values of the calculated squared atomic coefficients, in addition to the  $a_N$  constant, two equally large hyperfine constants  $a_H$  should be expected for **1**<sup>-</sup>, instead of only one large value, as observed. This discrepancy might cast some doubt on the assigned structure of the radical detected by us.

In trying to reconcile our assignments with theory, one should bear in mind that the reported LUMO coefficients refer to dye **1** in the gas phase. As discussed before, in a polar solvent such as DMSO the solvated dye should have a more polarized structure, like **1a** or **1b**, which were generated by positioning a +2 charge in the vicinity of the nitro group. If we calculate the LUMO densities of structure **1a**, which represents an intermediate situation between the non-polar structure **1** and the highly polarized structure **1b**, we arrive at the values shown in the structure, which are now qualitatively closer to the assigned values for the hyperfine constants.



An ambiguity persists as to the  $a_H$  constant of 0.20 mT, which we assigned to the hydrogen atom attached to C-3 and which, according to our calculations, corresponds to that attached to C-3'. This, however, does not invalidate the assigned structure of the detected radical. Our calculations are compatible with one nitrogen atom with high spin density ( $a_N = 0.90$  mT,  $c_{N^2} = 0.14$ ), and another large hydrogen hyperfine constant ( $a_H = 0.81$  mT,  $c_{C-4^2} = 0.15$ ). Besides these larger values, an intermediate hydrogen constant ( $a_H = 0.06$  mT,  $c_{C-3^2} = 0.06$ ) and two smaller values ( $a_H = 0.05$  and 0.03 mT,  $c_{C-3^2} = 0.006$  and  $c_{C-4^2} = 0.0005$ ) were observed, in agreement with our calculations.

The poor agreement between the spin densities of **1**<sup>-</sup> and the LUMO coefficients of the non-polar structure **1**, together with the fact that a closer match with theory was obtained when the polar structure **1a** was considered, validate the above model for mimicking the variable polarity of the medium through charges or 'sparkles' positioned in the vicinity of the molecule. In spite of being arbitrary, our model proved capable of generating a polarized structure with an electronic distribution compatible with the EPR hyperfine constants of the radical anion of **1**.

In conclusion, the electrochemical behaviour of the solvatochromic bithiophene dye **1** in various solvents was studied by CV and EPR techniques. The observed quasi-reversible and sometimes irreversible processes made difficult the search for correlations between the potentials obtained and the dipolarity-polarizability values of the solvent. The sensitivities of both the one-electron oxidation and the reduction potentials towards the solvent polarity were about the same. Quasi-reversible  $E_{ox}/E_{red}$  values decreased with the increased  $\pi^*$  values of the medium, a trend which was in agreement with the fact that charged species were generated from a neutral molecule. The generated radical anion of **1** could be detected by EPR and the resulting spectrum analysed to yield hyperfine coupling constants which suggest a heavy electron concentration on the nitrothienyl moiety of the radical. Unlike other bithienyl radicals with two electron-withdrawing substituents, the radical anion derived from **1** exhibited a much smaller barrier to rotation, indicated by line broadening of its EPR spectrum at room temperature. This difference is accounted for by the result of two opposing effects, arising from conjugation of the two rings: on the one hand this conjugation in the radical anion from **1** has the effect of increasing the double-bond character of the interannular link between the two rings, thereby preventing rotation; on the other hand, conjugation results in a

destabilizing electronic repulsion between the donor fragment and the added electron.

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