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Bis[bis-(4-alkoxyphenyl)amino] Derivatives of Dithienylethene, Bithiophene, Dithienothiophene and Dithienopyrrole: Palladium-Catalysed Synthesis and Highly Delocalised Radical Cations

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Abstract: Five diamines with thiophene-based bridges—(*E*)-1,2-bis-{5-[bis(4-butoxyphenyl)amino]-2-thienyl}ethylene (**1**), 5,5′-bis[bis(4-methoxyphenyl)amino]-2,2′-bithiophene (**2**), 2,6-bis[bis(4-butoxyphenyl)amino]dithieno[3,2-*b*:2′,3′-*d*]thiophene (**3**), *N*-(4-*tert*-butylphenyl)-2,6-bis[bis(4-methoxyphenyl)amino]dithieno[3,2-*b*:2′,3′-*d*]pyrrole (**4a**) and *N*-*tert*-butyl-2,6-bis[bis(4-methoxyphenyl)amino]dithieno[3,2-*b*:2′,3′-*d*]pyrrole (**4b**)—have been synthesised. The syntheses make use of the palladium(0)-catalysed coupling of brominated thiophene species with diarylamines, in some cases accelerated by microwave irradiation. The molecules all undergo facile oxidation, **4b** being the most readily oxidised at about −0.4 V versus ferrocenium/ferrocene, and solutions of the corresponding radical cations were generated by addition of tris(4-bromophenyl)aminium hexachloroantimonate to the neutral species. The near-IR spectra of the radical cations show absorptions characteristic of symmetrical delocalised species (that is, class III mixed-valence species); analysis of these absorptions in the framework of Hush theory indicates strong coupling between the two amine redox centres, stronger than that observed in species with phenylene-based bridging groups of comparable length. The strong coupling can be attributed to high-lying orbitals of the thiophene-based bridging units. ESR spectroscopy indicates that the coupling constant to the amino nitrogen atoms is somewhat reduced relative to that in a stilbene-bridged analogue. The neutral species and the corresponding radical cations have been studied with the aid of density functional theory and time-dependent density functional theory. The DFT-calculated ESR parameters are in good agreement with experiment, while calculated spin densities suggest increased bridge character to the oxidation in these species relative to that in comparable species with phenylene-based bridges.

Keywords: amination • electron spin resonance • mixed-valent compounds • oxidation • radicals

Introduction

Compounds containing two or more diarylamino redox groups have recently attracted attention as systems for studying electronic coupling and delocalisation.

The radical cations are mixed-valence (MV) compounds and typically show NIR intervalence charge-transfer (IVCT) bands; this terminology reflects the fact that in a valence-localised cation—that is, in a MV compound belonging to Robin and Day's class II[1]—the transition is related to electron-transfer from one redox site to the other, although the terminology is also commonly applied to delocalised (class III MV) systems, since the adiabatic states involved can be considered as arising from the same diabatic surfaces. IVCT absorptions have been analysed in the framework of Marcus–Hush theory[2] for radical cations of species in which diarylamino groups are linked by bridging groups based variously on benzene and other arenes,[3–5] biphenyl and other oligophenylenes,[3,6–8] phenylene-ethynylene,[3,9] phenylene-ethenylene,[10,11] cyclophanes,[12] organoplatinum[13] and phosphonium[14] moieties.

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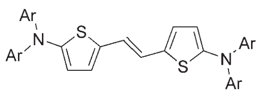
Although the NIR spectra of the radical cations of 5,5′-bis(diphenylamino)[2,2′]bithiophene[15] (**IVb**$^+$, see below) and of 5,5″-bis[4-(bis-4-tolylamino)phenyl][2,2′;5′,2]terthiophene[16] have been reported, and the radical cations of bis-[bis-(4-methoxyphenyl)amino]oligothiophenes have been studied computationally,[17] we are not aware of a detailed experimental investigation from the standpoint of mixed valency of a bis(diarylamino) system with a thiophene-based bridge.[18] Here we investigate the extent to which the lower ionisation potential of thiophene versus benzene (8.9 eV[19] versus 9.24 eV[20]) can lead to more effective mediation of coupling between two diarylamino groups in radical cation species with thienylene-based bridges than in analogous species with phenylene-based bridges; increased coupling has previously been found for bis(diarylamino) derivatives in which phenylene units of bridging groups are replaced by donor-substituted phenylene groups.[9] Stronger donor–acceptor coupling in thienylene-bridged dipolar chromophores than in phenylene analogues—as shown, for example, in first hyperpolarisability data[21]—has been attributed to the reduced aromatic character of thiophene; this may also potentially play a role in MV species. Somewhat reduced steric hindrance in the thiophene-based species may also lead to better π overlap between nitrogen- and bridge-based orbitals than in the phenylene analogues.[22]

Specifically, we report the synthesis and spectra of new bis(diarylamino) systems with thiophene-containing bridges: (*E*)-1,2-bis{5-[bis(4-butoxyphenyl)amino]-2-thienyl}ethylene (**1**), 2,6-bis[bis(4-methoxyphenyl)amino]-2,2′-bithiophene (**2**), 2,6-bis[bis(4-butoxyphenyl)amino]dithieno[3,2-*b*:2′,3′-*d*]thiophene (**3**), *N*-(4-*tert*-butylphenyl)-2,6-bis[bis(4-methoxyphenyl)amino]dithieno[3,2-*b*:2′,3′-*d*]pyrrole (**4a**) and *N*-*tert*-butyl-2,6-bis[bis(4-methoxyphenyl)amino]dithieno[3,2-*b*:2′,3′-*d*]pyrrole (**4b**).[23] We show that analysis of the NIR spectra of the corresponding radical cations in the framework of Hush theory[2] gives couplings in thienylene-based systems about 1.5 to 1.8 times greater than in phenylene-based analogues. Finally, we report the ESR spectra of the radical cations, which show well resolved hyperfine coupling; in combination with DFT calculations, these couplings give insight into the spin distribution in the radical cations and indicate that the increased effective coupling in the thienylene-based systems is accompanied by increased bridge character to the oxidation.



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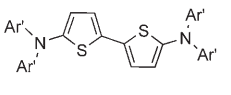

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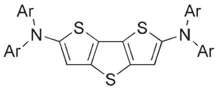

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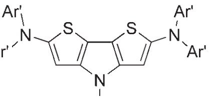


Ar = 4-nBuOC$_6$H$_4$
Ar' = 4-MeOC$_6$H$_4$

4a: R = 4-tBuC$_6$H$_4$
4b: R = tBu

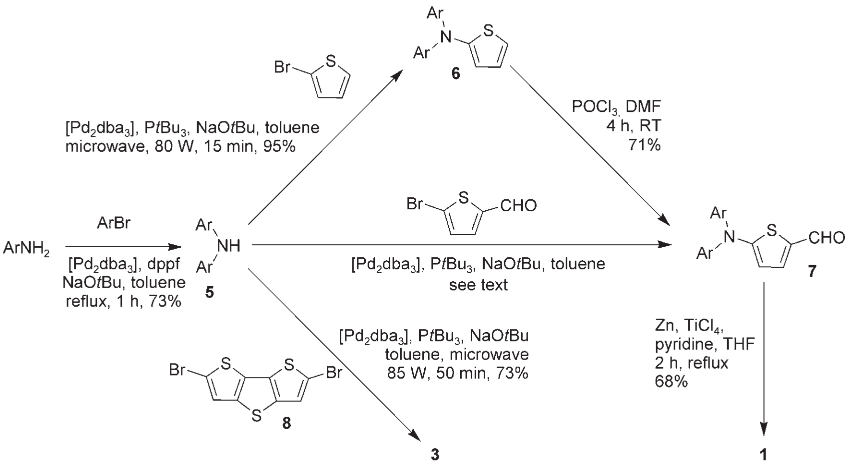
Results and Discussion

Synthesis: Our syntheses of compounds **1**–**4** (Schemes 1 and 2; see Supporting Information for full details) make extensive use of palladium-catalysed aminations. Bis(4-butoxyphenyl)amine (**5**), an intermediate common to the synthesis of both **1** and **3**, was obtained from 1-bromo-4-butoxybenzene and 4-butoxyaniline under coupling conditions similar to those reported for the synthesis of bis(4-methoxyphenyl)amine.[24] With conventional heating the reaction was complete after 1 hour; the product was obtained in good yield after recrystallisation (73 % versus the yield of 89 % reported for bis(4-methoxyphenyl)amine after 3 h heating[24]). We also carried out the synthesis of **5** with single-mode microwave irradiation; however, this offered no particular advantage over conventional heating, giving a slightly lower yield and only a slightly reduced reaction time.

Although 2-(diarylamino)-3,4-diarylthiophenes have also been obtained from reactions that involve cyclisation to form the thiophene ring and utilise diarylamide or thioamide starting materials,[25] most published syntheses of 2-(diarylamino)thiophene derivatives have involved coupling of a diarylamine with a 2-halothiophene. Diphenylamine has been coupled with 2-halothiophenes, in the presence of a palladium source (Pd(OAc)$_2$[26,27] or [Pd$_2$dba$_3$] {dba = dibenzylideneacetone}[26]) in conjunction with PtBu$_3$ (36–78 % from 2-bromothiophene[26–28]), or by use of CuI-mediated modified Ulmann conditions (40 % yield from 2-iodothiophene).[29] Various other diarylamines including bis(4-alkoxyphenyl)amines have been coupled with α,α′-dibromooligothiophenes and with 1,3-bis(5-bromothien-2-yl)benzo[*c*]thiophene in moderate yields in the presence either of Pd(OAc)$_2$/PtBu$_3$[30] or of [Pd(dppf)Cl$_2$]/dppf {dppf = 1,1′-bis(diphenylphosphino)ferrocene}[31] as catalysts.

Initially we attempted the coupling of **5** with 2-bromothiophene in the presence of Pd$_2$dba$_3$/dppf as the catalyst but observed no evidence for the formation of 5-[bis(4-butoxyphenyl)amino]thiophene (**6**); however, we successfully obtained **6** after changing the catalyst to Pd$_2$dba$_3$/PtBu$_3$. We carried out the reaction both with conventional heating and with a microwave reactor; after a few attempts at optimisation of the conditions we found that microwave heating could produce the desired product **6** in higher yields (95 %) than conventional heating (73 %) and that fewer byproducts were obtained under microwave conditions, which facilitated chromatographic isolation of the desired product (an oil). Consequently, we used microwave irradiation as the heating source for many of our subsequent reactions with 2-bromothiophene derivatives.[32] From **6**, 5-[bis-(4-butoxyphenyl)amino]-2-formylthiophene (**7**) was readily obtained in good yield under Vilsmeier conditions, affording the pure product in 71 % yield. Compound **7** can also be synthesised directly through the coupling of **5** with 2-bromo-5-formylthiophene in the presence of a Pd$_2$dba$_3$/PtBu$_3$ catalyst; however, we found that the desired aldehyde **7** was accompanied by a significant amount of the decarbonylated product **6**. Compound **7** was reductively coupled under McMurry conditions to give the target **1** in moderate yield.

In addition to its role as an intermediate in the synthesis of **1**, **7** is also of interest as a potential π-donor for dipolar chromophores, such as those used for electrooptic applications. Chromophores incorporating diarylamino-based donors generally show superior thermal and photochemical stability to their dialkylamino analogues;[33,34] calculations suggest that bis(4-alkoxyphenyl)amino-based donors show π-donor strength comparable to that of dialkylamino-based analogues,[35] and experimental[21] and theoretical[35] work suggests that the presence of the thienylene ring should lead to stronger donor–acceptor coupling than in phenylene analogues.

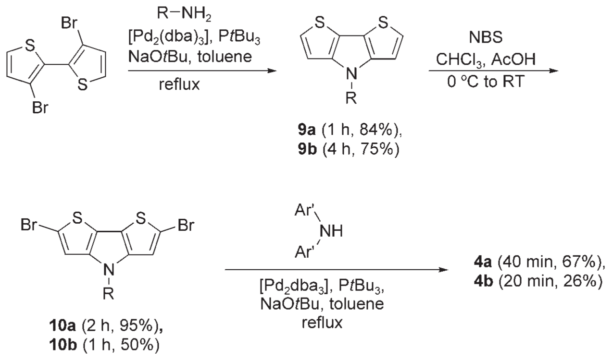


Scheme 1. Synthesis of compounds **1** and **3** (Ar = 4-*n*BuOC$_6$H$_4$).

Compound **3** was obtained in good yield as a glassy solid from the microwave-assisted palladium-catalysed coupling of **5** with 2,6-dibromodithieno[3,2-*b*:2′,3′-*d*]thiophene (**8**),[36] which was prepared by bromination of the parent dithieno[3,2-*b*:2′,3′-*d*]thiophene[37] with *N*-bromosuccinimide in $CHCl_3$/AcOH. The same reagents were used to synthesise the previously reported compound **2**[30] from 5,5′-dibromo-2,2′-bithiophene and bis(4-methoxyphenyl)amine in higher yield (76 % versus 27 %) than previously reported with use of $Pd(OAc)_2$/P*t*Bu$_3$.

N-Aryldithieno[3,2-*b*:2′,3′-*d*]pyrroles have previously been obtained by coupling of 3-bromothiophene with anilines to produce *N*,*N*-bis(3-thienyl)anilines, followed by bromination and copper-mediated coupling,[38] or by the palladium-catalysed coupling of 3,3′-dibromo-2,2′-bithiophene[39] with anilines (35 % over 50 h for aniline).[40,41] We chose the second route as the intermediate 3,3′-dibromo-2,2′-bithiophene can also be used for the synthesis of other *N*-substituted dithieno[3,2-*b*:2′,3′-*d*]pyrrole derivatives; by using an increased reaction temperature (reflux rather than 80 °C) we were able to obtain high yields of the *N*-(4-*tert*-butylphenyl) derivative **9a** in one hour. The *N*-*tert*-butyl derivative **9b** was also synthesised by the palladium-catalysed coupling of the appropriate amine with 3,3′-dibromo-2,2′-bithiophene; we were unable to obtain this product using conditions previously reported for *n*-alkylamines,[42] but obtained **9b** in good yield when P*t*Bu$_3$ was used in place of BINAP {BINAP = 2,2′-bis(diphenylphosphino)-1,1′-binaphthalene}.

Treatment of **9a** and **9b** with *N*-bromosuccinimide in $CHCl_3$/AcOH gave **10a** and **10b**, respectively, which, to the best of our knowledge, are the first reported examples of 2,6-dibromo-dithieno[3,2-*b*:2′,3′-*d*]pyrroles. It is worth noting that while the reaction was successful for *N*-aryl and *N*-*tert*-butyl species, analogues of **10a** and **10b** with *n*-alkyl *N*-substitution decomposed under these conditions with no dibromo derivative isolable; presumably the presence of the CH group α to N in the *n*-alkyl derivatives plays a role in these decompositions. Compounds **10a** and **10b** were converted into **4a** and **4b**, respectively, with the same catalyst system that was used to form **2** and **3**.



Scheme 2. Synthesis of bis(diarylamino)dithienopyrroles **4a** and **4b** (Ar′ = MeOC$_6$H$_4$; R = 4-*t*BuC$_6$H$_4$ for **4a**, **9a** and **10a**; R = 4-*t*Bu for **4b**, **9b** and **10b**).

Electronic spectra of the neutral species: The UV/visible spectra of the neutral species **1**, **2**, **3** and **4a** (**4b** has a very similar spectrum to **4a**) are compared in Figure 1. The data for the lowest-energy transitions are summarised in Table 1 including transition dipole moments μ_{ge}, which were obtained, in Debye, from integration of the spectra according to Equation (1), where $\tilde{\nu}$ and $\varepsilon(\tilde{\nu})$ are in cm^{-1} and $\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$, respectively.

$$\mu_{\mathrm{ge}} = 0.09584\sqrt{\int \frac{\varepsilon(\tilde{\nu})}{\tilde{\nu}}\,\mathrm{d}\tilde{\nu}} \approx 0.09584\sqrt{\frac{\int \varepsilon(\tilde{\nu})\,\mathrm{d}\tilde{\nu}}{\tilde{\nu}_{\max}}} \qquad (1)$$

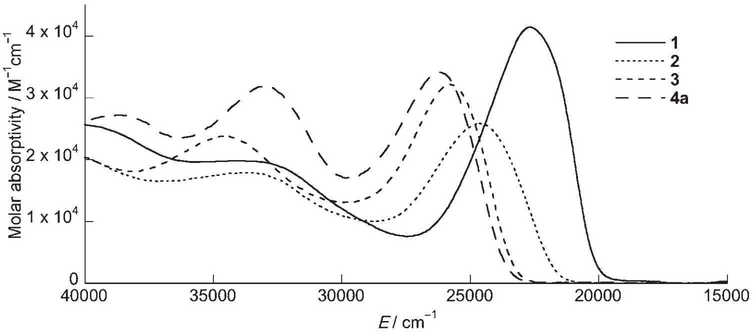


Figure 1. UV/visible absorption spectra for **1**, **2**, **3**, and **4a** in dichloromethane.

Table 1. Absorption maxima, absorptivities and transition dipole moments for the lowest-energy absorptions of the neutral compounds **1**, **2**, **3**, **4a** and **I** in dichloromethane with TD-DFT gas-phase values[a] in italics.

Compound	$\tilde{\nu}_{max}$ [cm^{-1}]		ε_{max} [M^{-1} cm^{-1}]	μ_{ge} [D]	
1	22600	*20500*	41400	8.58	*11.9*
2	24600	*22400*	25800	6.57	*9.03*
3	25800	*23800*	32100	7.31	*8.79*
4a	26200	*24300*	34100	7.62	*8.31*
I	25100[b]	*23100*	54900[b]	10.0[b]	*12.2*

[a] Computed with TD-DFT at the B3LYP/6-31G(d,p) level. [b] Data from ref. [10].

Data for the previously reported (*E*)-4,4′-bis[bis(4-methoxyphenyl)amino]stilbene (**I**, see below)[10] are also included for comparison. Table 1 also includes absorption maxima and transition dipole moments obtained by use of time-dependent density functional theory (TD-DFT) for gas-phase **1**, **2**, **3**, **4a** and **I** (*n*Bu and *t*Bu groups replaced by Me).

The TD-DFT calculations (see Supporting Information for details) show that the lowest-energy transition for each system is predominately a direct HOMO to LUMO excitation. The molecular orbitals involved in the transition are shown for each molecule in Figure 2, along with the HOMO−1, which is important in the spectra of the radical cations (see below). In each case the HOMO and HOMO−1 are of opposite parity and can be regarded as in- or out-of-phase linear combinations of two diarylamine-based orbitals (dominated by nitrogen p orbitals). The HOMO orbital, in particular, has significant bridge-based contributions from the local HOMO of the bridge, out of phase with those from the diarylamine-based orbitals. The LUMO in each case is principally bridge-based, resembling the LUMO of the isolated bridging moiety. The calculated energies compare well with the experimental data, although they are systematically underestimated by about 2000 cm^{-1} (this corresponds to less than 10 % of the actual transition energy). The lowest-energy transitions are seen for compound **1**, which is consistent with the expected effect of extending conjugation with a vinylene moiety. Compounds **3** and **4a** show very similar transition energies, which are blue-shifted relative to that of **2**; this is presumably partly attributable to the destabilising contributions to the LUMOs of **3** and **4a** from the central heteroatoms of the bridges. Both theory and experiment show larger transition dipole moments in the species with

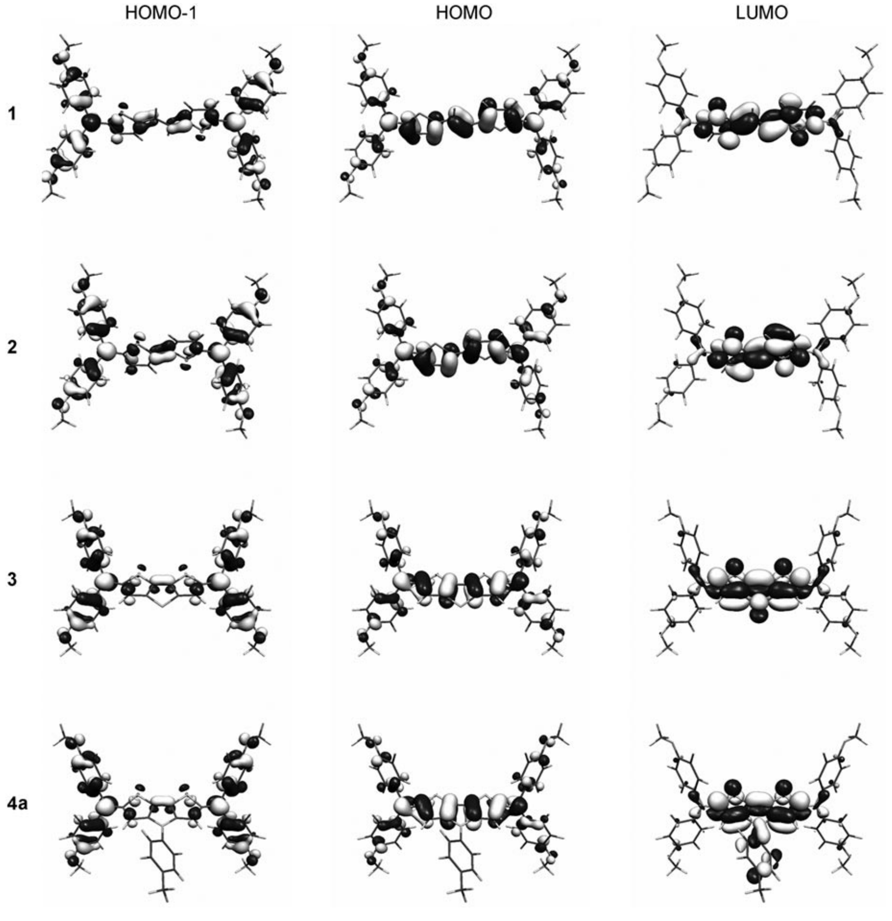


Figure 2. HOMO−1, HOMO and LUMO for **1**, **2**, **3** and **4a** according to DFT calculations at the B3LYP/6-31G(d,p) level.

more extended conjugation—the vinylene-bridged compounds **1** and **I**—than in **2**, **3** and **4a**, which is consistent with polarisation of the transition along the long axis between the two amine groups.

Electrochemistry: Cyclic voltammograms of **1**–**4** (Figure 3, Table 2) indicate that the five compounds each show two facile reversible oxidations. The table also includes redox potentials of related bis[bis(4-methoxyphenyl)amino] analogues with hydrocarbon bridges,[3,11,30] indicating **1**–**4** to be rather more readily oxidised than analogues with 1,4-phenylene, biphenyl-4,4′-diyl, or (*E*)-stilbene-4,4′-diyl bridges.[43] The dithienopyrrole-based bridges result in the most electron-rich compounds, which are about 0.2 V more readily oxidised than their dithienothiophene-bridged analogue, which is consistent with the ionisation potentials of the simple pyrrole (8.2 eV) and thiophene (8.9 eV) heterocycles,[19] with the *N*-alkyl derivative **4b** being slightly more electron-rich than its *N*-aryl analogue **4a**.

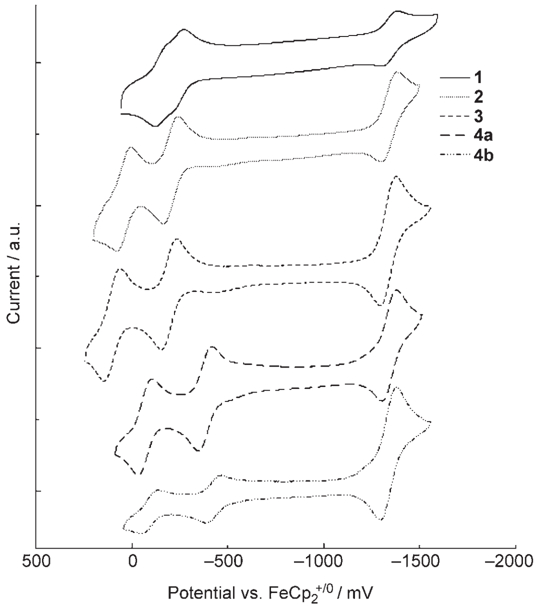


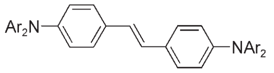
Figure 3. Cyclic voltammograms of **1**, **2**, **3**, **4a** and **4b** (CH_2Cl_2, 0.1 M $[nBu_4N]^+[PF_6]^-$, 50 mV s^{-1}) with $Cp_2Co^{+/0}$ as an internal reference (−1320 mV versus $FeCp_2^{+/0}$).

The separations between the first and second redox potentials ($\Delta E_{1/2}$) for all five compounds are greater in the less polar solvent, which is consistent with the predictions of the dielectric continuum model for the electrostatic contribution to $\Delta E_{1/2}$.[44] Although $\Delta E_{1/2}$ values have often been used as measures of the electronic coupling (V) between the diabatic states in the MV species, it has been shown that they provide a very poor guide and must be used with extreme caution;[45] indeed, the values of $\Delta E_{1/2}$ in Table 2 show no clear relation with the spectroscopic estimates of V given for **1**$^+$–**4a**$^+$, **I**$^+$, **IIa**$^+$ and **IIIa**$^+$ in Table 3 (see below). However, it is worth noting that the $\Delta E_{1/2}$ values for **3**, **4a** and **4b** are rather large compared to many of the other species included in the table, indicating that the corresponding radical cations are relatively stable to disproportionation.

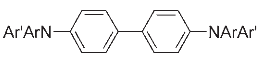
Table 2. Redox potentials for bis[bis(4-alkoxyphenyl)amino] compounds versus $FeCp_2^{+/0}$ determined by cyclic voltammetry in 0.1 M $[nBu_4N]^+[PF_6]^-$.

	CH_2Cl_2			CH_3CN		
Compound	$E_{1/2}^{+/0}$	$E_{1/2}^{2+/+}$	$\Delta E_{1/2}$	$E_{1/2}^{+/0}$	$E_{1/2}^{2+/+}$	$\Delta E_{1/2}$
1	−0.23	−0.14	0.09	−0.22[a]		[a]
2[b,c]	−0.20	−0.04	0.16	−0.14	−0.02	0.12
3	−0.19	+0.13	0.32	−0.19	+0.03	0.22
4a	−0.40	−0.08	0.32	−0.31	−0.07	0.24
4b	−0.43	−0.10	0.33	−0.37	−0.15	0.22
I[d]	+0.08	+0.22	0.14	–	–	–
IIa[e]	+0.09	+0.31	0.22	–	–	–
IIIa[e]	−0.15	+0.34	0.49	–	–	–

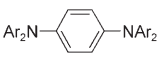
[a] Separation not resolvable. [b] Values for **2** in MeCN/0.1 M $[nBu_4N]^+[PF_6]^-$ reported in ref. [30] are similar. [c] Potentials for **IVa**, **IVb** and longer Ph-terminated species in PhCN/0.1 M $[nBu_4N]^+[PF_6]^-$ are reported in ref. [15]. [d] Data from ref. [10]. [e] Data from ref. [3].



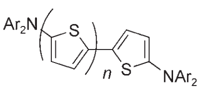
I: Ar = 4-MeOC$_6$H$_4$



IIa: Ar = Ar' = 4-MeOC$_6$H$_4$
IIb: Ar = Ph, Ar' = 2,4-Me$_2$C$_6$H$_3$



IIIa: Ar = 4-MeOC$_6$H$_4$
IIIb: Ar = Ph



IVa: *n* = 0, Ar = Ph
IVb: *n* = 1, Ar = Ph

Electronic spectra of the monocations 1$^+$–4$^+$: The radical cations of **1**–**4** were generated in dichloromethane solution by addition of an excess of the diamine to a solution of tris(4-bromophenyl)aminium hexachloroantimonate (see Supporting Information for details) as previously described for other diamines.[10,11,13] Figure 4 shows the Vis/NIR spectra of the resulting solutions, with the exception of that of **4b**$^+$ (shown in Supporting Information), which is essentially identical to that of **4a**$^+$. The insensitivity of the spectra of **4a**$^+$ and **4b**$^+$ to the substituent on the pyrrole nitrogen is consistent with the lack of pyrrole nitrogen contributions to the relevant orbitals (see Figure 2). Cations **1**$^+$–**4**$^+$ show intense absorption bands in the NIR region; these are similar in terms of energy, absorptivity, and lineshape to the intervalence charge-transfer (IVCT) absorptions previously observed for other strongly coupled bis(diarylamino) MV cations, data for some examples of which are also included in Table 3. Firstly, the observed bandwidths at half height ($\tilde{\nu}_{1/2[\text{obs}]}$) are narrower than the width predicted for a class II MV species by Equation (2) (which is written for the case in which both $\tilde{\nu}_{1/2[\text{Hush}]}$ and $\tilde{\nu}_{\max}$ are in cm^{-1}).

$$\tilde{\nu}_{1/2[\text{Hush}]} = \sqrt{(2310 \times \tilde{\nu}_{\max})} \qquad (2)$$

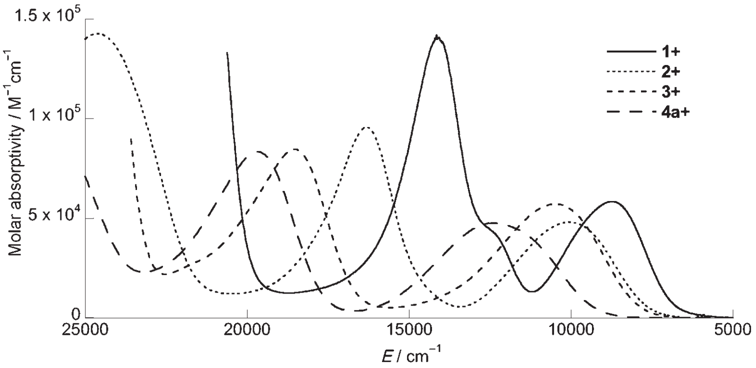


Figure 4. Visible/NIR spectra of monocations $\mathbf{1}^+$–$\mathbf{4a}^+$ in dichloromethane. The onsets of strong absorption at high energy (at ≈20000 for $\mathbf{1}^+$ and ≈23000 cm^{-1} for $\mathbf{2}^+$, $\mathbf{3}^+$ and $\mathbf{4a}^+$) correspond to absorption by the excess neutral diamines present; the absorptivity scale applies only to the lower energy absorptions attributable to the radical cations.

Secondly, for $\mathbf{1}^+$, $\mathbf{2}^+$ and $\mathbf{3}^+$ the bands are strongly asymmetric; following Lambert and Nöll, the asymmetry is quantified in Table 3 by the ratio $\tilde{\nu}_{1/2[\mathrm{high}]}/\tilde{\nu}_{1/2[\mathrm{low}]}$, where $\tilde{\nu}_{1/2[\mathrm{high}]}$ and $\tilde{\nu}_{1/2[\mathrm{low}]}$ are defined as twice the bandwidths on the high- and low-energy sides of the absorption maximum, respectively. The values of $\tilde{\nu}_{1/2[\mathrm{high}]}$ approach the Hush limit ($\tilde{\nu}_{1/2[\mathrm{Hush}]}$). In organic MV radical cations these spectral characteristics were originally interpreted in terms of a cut-off on the low-energy side of the band due to the thermal population of the electron-transfer barrier top;[3,46,47] according to this model, this situation is predicted for any system belonging to Robin and Day's class II[1] (valence-localised) but lying very close to the borderline with class III (delocalised): that is, with a low barrier to intramolecular electron transfer. Subsequent work suggested that these lineshapes could also arise from coupling of the electron transfer in class III and class II/class III borderline systems to symmetric vibrations.[48] A number of other bis(diarylamino) MV cations have been found to exhibit similar lineshapes; crystallographic and vibrational studies[4,6,11] and variable-temperature measurements of the IVCT band shapes[49] support the latter of the two interpretations. Although the NIR absorptions of $\mathbf{4a}^+$ and $\mathbf{4b}^+$ are also consistent with delocalised structures in that both $\tilde{\nu}_{1/2[\mathrm{obs}]}$ and $\tilde{\nu}_{1/2[\mathrm{high}]}$ are well below $\tilde{\nu}_{1/2[\mathrm{Hush}]}$, the bands are the broadest of the species under consideration ($\tilde{\nu}_{1/2[\mathrm{obs}]}$ over 600 cm^{-1} greater than for the next broadest—that of $\mathbf{3}^+$) and are considerably less asymmetric as gauged by $\tilde{\nu}_{1/2[\mathrm{high}]}/\tilde{\nu}_{1/2[\mathrm{low}]}$ (compare the values of 1.34 and 0.95 for $\mathbf{3}^+$ and $\mathbf{4a}^+$, respectively). Thus, the characteristics of the low-energy NIR absorptions strongly support the assignment of $\mathbf{1}^+$–$\mathbf{4}^+$ to Class III, along with the previously studied $\mathbf{I}^+$.

The DFT results for the $\mathbf{1}^+$, $\mathbf{2}^+$, $\mathbf{3}^+$, $\mathbf{4a}^+$ and $\mathbf{I}^+$ radical cations also suggest that all these systems should be assigned to class III. While use of DFT often affords overdelocalised structures and, therefore, may suggest a symmetric class III structure for a class II species, it has previously been found to give good agreement with structural and spectroscopic features when applied to species shown experimentally to belong to class III.[4,6,11] The DFT results show that **1**–**4** undergo similar geometric changes to **I** on oxidation (see Supporting Information for details): the N$-$C$_{\mathrm{bridge}}$ bonds contract (N$-$C$_{\mathrm{bridge}}$ bonds being shorter in **1**–**4** and $\mathbf{1}^+$–$\mathbf{4}^+$ than in **I** and $\mathbf{I}^+$, respectively), the N$-$C$_{\mathrm{aryl}}$ bonds lengthen, the bridge bond-length pattern shifts towards, but not fully to, a semi-quinoidal limit, the nonplanar bridges (those of **1**, **2**, and **I**) planarise, and the angle between the planes defined by the bridging groups and by the amine N atoms and the attached C atoms decreases (more dramatically and giving a smaller final angle in $\mathbf{1}^+$–$\mathbf{4}^+$ than in $\mathbf{I}^+$). The TD-DFT transition energies and transition dipole moments are included in Table 3. The calculated energies are slightly overestimated for the ethylene-bridged species $\mathbf{1}^+$ and $\mathbf{I}^+$ and slightly underestimated for $\mathbf{2}^+$ and for the fused-ring species $\mathbf{3}^+$ and $\mathbf{4a}^+$, with the variation in $\tilde{\nu}_{\mathrm{max}}$ between compounds being well reproduced; this further supports our assignment of the cations to class III. The transition dipole moments are generally less well reproduced by TD-DFT calculations than in the case of the corresponding neutral species.

Table 3. Parameters from the low-energy NIR absorptions of $\mathbf{1}^+$, $\mathbf{2}^+$, $\mathbf{3}^+$, $\mathbf{4a}^+$ and other symmetric bis[bis(4-alkoxyphenyl)amino] radical cations in CH_2Cl_2 or, for $\mathbf{IIa}^+$ and $\mathbf{IIIa}^+$, CH_2Cl_2/0.1 mM $[n\mathrm{Bu_4N}]^+[\mathrm{PF_6}]^-$, with some values from TD-DFT calculations[a] in italics.

	$\tilde{\nu}_{\mathrm{max}}$ [cm^{-1}]		$\varepsilon_{\mathrm{max}}$ [M^{-1} cm^{-1}]	$\tilde{\nu}_{1/2[\mathrm{obs}]}$ [cm^{-1}]	$\tilde{\nu}_{1/2[\mathrm{Hush}]}$[b] [cm^{-1}]	$\tilde{\nu}_{1/2[\mathrm{high}]}$/ $\tilde{\nu}_{1/2[\mathrm{low}]}$[c]	$\tilde{\nu}_{1/2[\mathrm{high}]}$/ $\tilde{\nu}_{1/2[\mathrm{Hush}]}$[d]	μ_{ge} [D]		$V_{[\mathrm{Eq.\,(3)}]}$[e] [cm^{-1}]	$V_{[\mathrm{Eq.\,(4)}]}$ [cm^{-1}]
$\mathbf{1}^+$	8750	*9480*	56500	2720	4500	1.37	0.70	13.0	*9.3*	2150	4375
$\mathbf{2}^+$	10100	*10020*	47900	3338	4830	1.17	0.75	12.3	*9.6*	2820	5050
$\mathbf{3}^+$	10500	*10300*	57100	3640	4920	1.34	0.85	14.0	*10.4*	3400	5250
$\mathbf{4a}^+$	12500	*11600*	49000	4260	5370	0.95	0.77	12.3	*9.7*	3480	6270
$\mathbf{I}^+$	6080[f]	*6980*	39300[f]	2760[f]	3750	1.40[f]	0.86	13.5[f]	*15.5*	1400	3020
$\mathbf{IIa}^+$	6360[g]	*6920*[h]	28000[g]	3170[g]	3830	1.45[g]	0.98	11.6[g]	*14.5*[h]	1550	3180
$\mathbf{IIIa}^+$	9350[g]	*9250*[h]	22700[g]	3640[g]	4650	1.76[g]	0.99	9.17[g]	*10.1*[h]	3240	4675

[a] B3LYP/6-31G(d,p) level. [b] Calculated using Equation (2). [c] Ratio of bandwidth on high-energy side to that on low-energy side. [d] Ratio of twice the band on the high-energy side to the bandwidth from Equation (2). [e] Estimated from Equation (3) using the experimentally determined values of $\tilde{\nu}_{\mathrm{max}}$ and μ_{ge} and the geometric N–N distance. [f] Data taken from refs. [10,11]. [g] Data from ref. [3]. [h] TD-DFT values from ref. [48].

According to DFT calculations, the molecular orbitals of the radical cations very closely resemble those of the corresponding neutral species, with the semi-occupied orbitals of the radical ions corresponding to the HOMOs of the neutral species (Figure 2). In the nomenclature of the neutral molecules, the TD-DFT results indicate that the lowest-energy transition of the radical cations is predominantly HOMO−1 to HOMO in nature, with other configurations playing a slightly more important role in the more extended species. Thus, the transition is between combinations of diarylamino-based orbitals (dominated by amine nitrogen p orbitals) with opposite parity, this orbital picture closely resembling that previously reported for other delocalised bis(diarylamino) radical cations,[4,6,15–17,50] and thus suggesting that the lowest energy bands of **1**$^+$–**4**$^+$ have significant IVCT character.

The electronic structure calculations also provide some insight into the differences in experimentally observed band shapes. The relaxation energy associated with the lowest excited state of the radical cations was estimated by the symmetry-constraint approach.[48] The relaxation energies were estimated by DFT to be 2873 cm^{-1}, 3480 cm^{-1}, 3331 cm^{-1} and 3943 cm^{-1} for **1**$^+$, **2**$^+$, **3**$^+$ and **4a**$^+$, respectively, and thus follow the trend seen in the experimentally measured values of $\tilde{\nu}_{1/2[\text{obs}]}$ (2720, 3338, 3640, and 4260 cm^{-1}, respectively). Therefore, the increase in bandwidth on going from **3**$^+$ to **4a**$^+$ could be related to a significant (about 600 cm^{-1}) increase in the corresponding relaxation energy. Usually, larger relaxation energies result in a more symmetric (Gaussian-like) band shape; this is consistent with the broader, more symmetric, lineshape of the IVCT of **4a**$^+$ relative to that of **3**$^+$.

Electronic coupling: According to Hush theory,[2] the electronic coupling (V) between two redox centres can be obtained from the transition dipole moment (μ_{ge}) and the absorption maximum ($\tilde{\nu}_{\text{max}}$) of the IVCT band of the MV species according to Equation (3) in which e is the electronic charge and R is the diabatic electron-transfer distance; that is, the distance between donor and acceptor in the absence of any electronic coupling.

$$V = \mu_{\text{ge}}\tilde{\nu}_{\text{max}}/(eR) \tag{3}$$

In the case of Class III MV systems, the coupling can also be obtained directly from the IVCT maximum by using Equation (4).

$$V = \tilde{\nu}_{\text{max}}/2 \tag{4}$$

Estimates of V from Equation (3), obtained by assuming R to be the geometric N–N separation, are given in Table 3, along with values from Equation (4). According to either estimate, **1**$^+$, **2**$^+$, **3**$^+$ and **4a**$^+$ all show rather large couplings, as would be anticipated from the electron-rich character of the thiophene-containing bridges. Comparison of the dithienylethylene derivative with the stilbene species, **1**$^+$ and **I**$^+$, or of the bithiophene and biphenyl species, **2**$^+$ and **IIa**$^+$, respectively, shows that replacement of phenylene with thienylene groups leads to increased coupling. The coupling suggested by Equation (4) in the dithienopyrrole-bridged species **4a**$^+$ is the strongest yet reported for a bis[bis(4-alkoxyphenyl)amino] MV species, including **IIIa**$^+$ (a stronger coupling of $V_{[\text{Eq. (4)}]} = 5790$ cm^{-1} is obtained for the 1,4-bis(diphenylamino)benzene radical cation **IIIb**$^+$,[4] emphasising that the *relative* electron-richness of the bridge and the end groups is important, while a value of $V_{[\text{Eq. (4)}]} = \approx 5550$ cm^{-1} for **IVb**$^+$ can be deduced from the published spectrum[15]). For all the compounds in Table 3 the couplings estimated according to Equation (3) are significantly smaller than those obtained from Equation (4). This discrepancy is at least partly attributable to the N–N separation being greater than the true diabatic electron-transfer distance; that is, the redox centres cannot be regarded as centred on the N atoms, but are displaced somewhat into the bridge. Assuming the validity of Equations (3) and (4),[51] the appropriate values of R would have to be approximately half to two-thirds of the geometric N–N separation. In view of the reduced diabatic electron-transfer distances in all these species, it is interesting to ask to what extent these species can still be regarded as diamino MV species, rather than being "bridge-oxidised" species. To obtain information pertinent to this question, we turn next to examine the electron-spin resonance (ESR) spectra of the monocations.

Electron-spin resonance of monocations: Room temperature X-band ESR spectra were acquired for the same CH_2Cl_2 solutions of **1**$^+$–**4**$^+$ as used for measurement of the Vis/NIR spectra; the spectra show more resolvable coupling than the spectra of bis(diarylamino) MV species that we have previously reported.[10,11,13] The spectra are shown in Figure 5 (as in the case of the optical spectra, the ESR spectrum of **4b**$^+$ is shown only in the Supporting Information, due to its close similarity to that of **4a**$^+$). The spectra are reminiscent of those of the radical cations of bis(diphenylamino)-terminated oligothiophenes such as **IVa**$^+$ and **IVb**$^+$, in which coupling constants to the $I = 1$ ^{14}N and the $I = \frac{1}{2}$ ^{1}H of the bridging ligand are of comparable magnitude.[15] Figure 5 shows the spectra, along with the previously report-

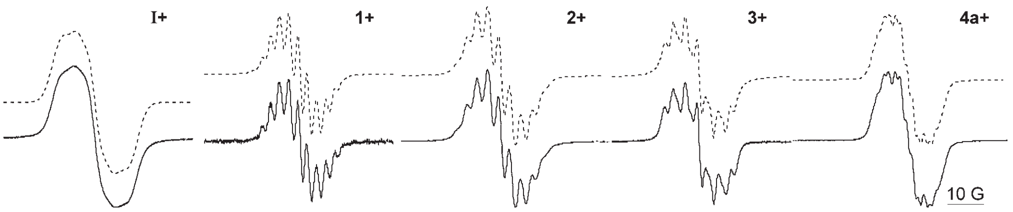


Figure 5. Experimentally observed X-band ESR spectra (lower, solid line) of **I**$^+$ and **1**$^+$–**4**$^+$ in dichloromethane with simulations (upper, dotted lines) used to obtain coupling constants.

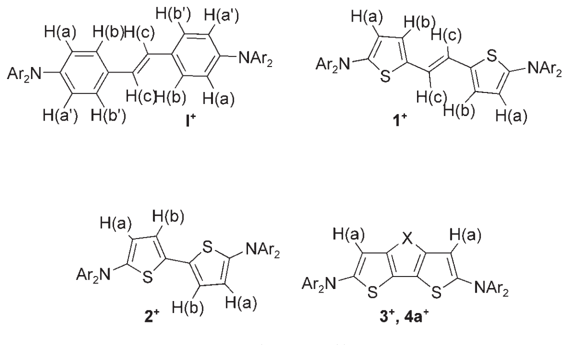
ed spectrum of $\mathbf{I}^+$,[11] and spectra simulated using WinSim.[52,53] In all cases, the spectra are centred at $g = 2.004$, a typical value for triarylamine radical cations.[54] In all cases the spectra were fitted by assuming coupling to two equivalent ^{14}N nuclei, to varying numbers of pairs of ^{1}H nuclei, and the to the pyrrole ^{14}N of $\mathbf{4a}^+$ (i.e., with the cations assumed to be symmetrical, at least on a timescale of $>10^{-7}$ s).[55] The coupling constants obtained from the simulations are given in Table 4; values obtained from DFT calculations, also given in the table, are in good agreement with the experimental data, and allow us to assign the resolvable ^{1}H coupling, as indicated in Table 4 and in Scheme 3. Moreover, the good agreement between experimentally measured and DFT-calculated coupling constants suggests that DFT describes the spin distribution in the radical cations well and, therefore, suggests that we are justified in using DFT spin densities as a means of assessing the degree to which the oxidation can be regarded as amine-based (see below).

Table 4. Experimentally observed and theoretical (italics) ESR hyperfine coupling constants (G) for some bis[bis(4-alkoxyphenyl)amino] radical cations.[a]

	$\mathbf{1}^+$		$\mathbf{2}^+$		$\mathbf{3}^+$		$\mathbf{4a}^+$		$\mathbf{I}^+$	
$A_{N(a)}$	2.68	*2.91*	3.20	*3.32*	3.44	*3.43*	3.17	*3.15, 3.18*	3.80[c]	*3.65*
$A_{H(a)}$[b]	2.00	*−1.90*	2.70	*−2.51*	2.15	*−1.85*	1.24	*−1.17, −1.20*	[d]	*−0.76, −0.82*[e]
$A_{H(b)}$[b]	2.28	*−2.09*	2.20	*−2.15*	–	–	–	–	[d]	*−0.26, −0.30*[e]
$A_{H(c)}$[b]	1.90	*−1.79*	–	–	–	–	–	–	[d]	*−1.48*
$A_{N(b)}$[f]	–	–	–	–	–	–	1.61	*−1.22*	–	–

[a] Isotropic Fermi contact couplings calculated at the open-shell B3LYP/6-31G(d,p) DFT level with both sign and magnitude; experimental values are moduli ($|A|$). [b] H(a), H(b) and H(c) are defined in Scheme 3. [c] We have previously reported[11] a somewhat larger value for this coupling constant by inspection of the experimentally measured spectrum; however, the spectra are better simulated with the present value. [d] Not resolvable in the experimentally measured spectrum. [e] The two values given are H(a), H(a′) or H(b), H(b′). [f] This nitrogen is that in the pyrrole ring of $\mathbf{4a}^+$.

A value of $A_N = 8.97$ G has been reported for $[(4\text{-}MeOC_6H_4)_3N]^+$ in MeCN;[56] thus, a notional class III (or rapidly exchanging) MV system consisting of two such redox centres would be expected to show $A_N = \approx 4.5$ G. The experimentally measured (and calculated) A_N values are lower, decreasing in the order $\mathbf{I}^+ > \mathbf{3}^+ > \mathbf{2}^+ > \mathbf{4a}^+ > \mathbf{1}^+$, suggesting that the total spin density for the two ^{14}N atoms is reduced relative to that in $[(4\text{-}MeOC_6H_4)_3N]^+$, which is consistent with the bridge character of the oxidation increasing in the order $\mathbf{I}^+ < \mathbf{3}^+ < \mathbf{2}^+ < \mathbf{4a}^+ < \mathbf{1}^+$. DFT-calculated spin densities (see Table 5) are consistent with this picture. Even in $\mathbf{I}^+$ there is considerably more spin density on the stilbene bridge than on the terminal aryl groups, which is consistent with the shift of the diabatic states into the bridge suggested by the NIR data (see above) and with the appearance of the partially occupied orbital (corresponding to the HOMO of the neutral species shown in Figure 2). In the thiophene-containing radical cations the spin density on the bridge is increased at the expense of that on N and that on the terminal aryl groups, with the bridge character increasing in the same order as deduced from the values of A_N. Nevertheless, the calculations indicate that the amino nitrogen atoms bear greater spin density than any of the other atoms, suggesting that, although the bridge character of the oxidation is increased in $\mathbf{1}^+$–$\mathbf{4}^+$ relative to that in analogues such as $\mathbf{I}^+$, the species with thiophene-based bridges can still be regarded as having significant MV diamine character.



Scheme 3. Labelling scheme for ^{1}H and ^{14}N nuclei for which coupling constants are given in Table 4.

Table 5. DFT-calculated spin densities for different portions of the radical cations $\mathbf{1}^+$, $\mathbf{2}^+$, $\mathbf{3}^+$, $\mathbf{4a}^+$ and $\mathbf{I}^+$.

	$\mathbf{1}^+$	$\mathbf{2}^+$	$\mathbf{3}^+$	$\mathbf{4a}^+$	$\mathbf{I}^+$
terminal aryl	0.12	0.15	0.17	0.13	0.27
amino N atoms	0.25	0.28	0.29	0.27	0.31
bridging group	0.63	0.57	0.54	0.60	0.42

Conclusions

Bis(4-alkoxyphenyl)amines can be coupled to bromothiophene and related derivatives in good yield under palladium-catalysed conditions; at least in some cases microwave irradiation leads to improved yields and fewer side reactions. Five bis[bis(4-alkoxyphenyl)amino] species with thiophene-based bridges have been synthesised. The ease of oxidation of these materials suggests that compounds of this type may have applications as hole-injection materials in organic light-emitting diodes, while the 5-[bis-(4-butoxyphenyl)-amino]-2-formylthiophene intermediate used in the synthesis of one of these compounds has potential utility as a potent π-donor for incorporation into stable electrooptic chromophores. The radical cations of the bis[bis(4-alkoxyphenyl)amino] compounds have been generated; their NIR spectra are indicative of strong coupling between the two redox centres, stronger than that observed in species with phenylene-based bridging groups of comparable length. This can be largely attributed to high-lying orbitals of the thiophene-based bridging units (steric factors may also contribute); indeed, ESR spectroscopy and quantum chemical calculations indicate increased spin density on the bridging groups than in comparable species with phenylene-based bridges, with a concomitant reduction in spin density on the amino nitrogen centres. However, the observed ESR coupling constants, the calculated spin densities and the calculated radical cation structures demonstrate that the amine nitrogen atoms still play a dominant role in the oxidation process; that is, that these cations can still be regarded as MV compounds, albeit with an appreciable bridge-based character.

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dation at −0.28 V versus $FeCp_2^{+/0}$ in CH_2Cl_2/0.1 M $[nBu_4N]^+[PF_6]^-$ (no separation between first and second oxidation processes was discernable). Thus, this species is slightly more easily oxidised than **1**–**3**, presumably due to the gain in aromaticity of the benzo ring of the bridging group on oxidation.

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