A mixed-valence bis(diarylamino)stilbene: crystal structure and comparison of electronic coupling with biphenyl and tolane analogues†

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The *E*-4,4′-bis[di(*p*-anisyl)amino]stilbene cation is a class-III mixed-valence species with electronic coupling comparable to that in its biphenyl-bridged analogue, whereas its tolane-bridged analogue belongs to class II.

Mixed-valence (MV) species based on triarylamine redox centers have recently attracted considerable interest.[1–5] However, assignment to Robin and Day's class II (valence-localised) or III (delocalised)[6] based on the characteristics of their intervalence charge-transfer (IVCT) bands can be problematic; for many examples, such as [2a]$^+$,[2] the IVCT bands show the intensity and asymmetry associated with class III species, yet are broad, suggestive of class II species. These lineshapes have variously been interpreted as indicating localised species close to the class II/III borderline,[2] and/or as arising from strong coupling of the electron transfer to symmetrical vibrations.[3a] [1]$^+$ and [2b]$^+$ have very recently been shown to be class III using vibrational spectroscopy.[4,5b] In contrast, the IVCT band of [3]$^+$ is strongly suggestive of class II.[2,3a] Here we report the first study of a vinylene-bridged bis(triarylamine) MV system, [4]$^+$; we have thoroughly characterised this cation, which shows an asymmetric IVCT band very similar to that of [2a]$^+$, and assign it to class III, in contrast to its class-II ethynylene-bridged analogue, [3]$^+$.
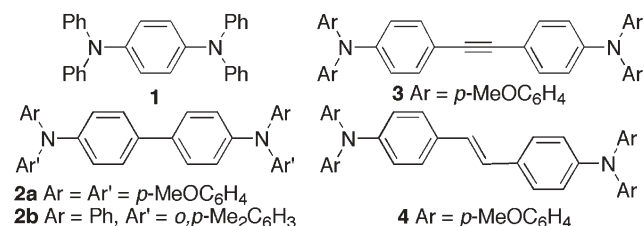
4 was synthesised using Pd^0-catalysed coupling of *E*-4,4′-dibromostilbene with bis(*p*-anisyl)amine.† Cyclic voltammetry in CH_2Cl_2 shows two successive reversible one-electron oxidations at *ca.* +0.08 and +0.22 V *vs.* FeCp$_2^{+/0}$; values of *ca.* +0.09, +0.31 V and +0.21, +0.36 V are reported for **2a** and **3** respectively.[2] Blue solutions containing [4]$^+$ were generated by treatment with sub-stoichiometric [(*p*-BrC$_6$H$_4$)$_3$N]$^+$[SbCl$_6$]$^-$;

red-brown solutions of [3]$^+$ were generated in the same way for comparison. [4]$^+$[SbF$_6$]$^-$ was isolated as golden-green crystals following oxidation of **4** with sub-stoichiometeric AgSbF$_6$ in CH_2Cl_2, filtration, and layering with Et$_2$O.

We have determined the structures of **4** and [4]$^+$[SbF$_6$]$^-$ at 120 K using X-ray diffraction.†‡ A view of the molecular structure of the [4]$^+$ cation is presented in Fig. 1. There are only two previous reports of X-ray studies of bis(triarylamine) MV cation salts.[4,5b] Neutral **4** has crystallographic C_i symmetry, but [4]$^+$ has no crystallographically imposed symmetry. However, both N–C$_{stilbene}$ bonds both shorten slightly on oxidation; moreover, the differences between N–C$_{stilbene}$ and N–C$_{anisyl}$ in [4]$^+$ support delocalisation; for a localised structure, one might expect three more-or-less similar bond lengths around the oxidised nitrogen, these being shorter than those at the other nitrogen. There are only slight changes in the vinylene unit on oxidation; this is similar to the situation in class III [2b]$^+$, where the central C–C bond of the biphenyl is similar to that in the neutral species.[5a] There is a quinoidal pattern of bond-length alternation (BLA) of 0.034(14) Å in the stilbene benzene rings of [4]$^+$, similar to the 0.042 Å found in DFT calculations[7] (in neutral **4**, BLA = 0.021(3) Å by X-ray, 0.021 Å by DFT). Similar values are seen in X-ray[5a] (0.032(12) Å) and DFT (0.03–0.04 Å) structures for 4,4′-bis(diarylamino)biphenyl radical cations[5a,8] (the experimental and computed BLAs in the bridge of [1]$^+$ are *ca.* twice as large).[7] Whilst the X-ray data are consistent with the assignment of [4]$^+$ to class III, they do not exclude the
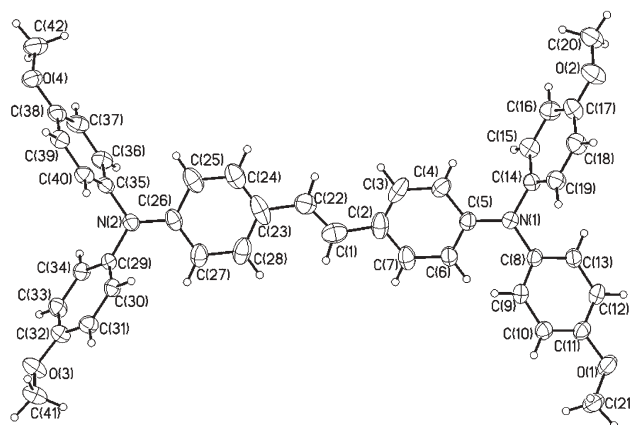

Fig. 1 A view of the [4]$^+$ cation from the crystal structure of its [SbF$_6$]$^-$ salt. Selected bond lengths (Å): N1–C5 1.377(4), N1–C8 1.424(4), N1–C14 1.427(4), N2–C26 1.361(4), N2–C29 1.434(4), N2–C35 1.437(4).

possibilities of a class II species with only slight asymmetry, or in which asymmetry is masked by static or dynamic disorder.

Both [3]⁺ and [4]⁺ appear delocalised on the EPR timescale,† but the IR spectrum of a CH_2Cl_2 solution of [3]⁺ shows a C≡C stretch at 2135 cm⁻¹, indicating a lack of inversion symmetry (no C≡C stretch is seen for centrosymmetric 3), *i.e.* that [3]⁺ belongs to class II. For [4]⁺, such a simple vibrational probe is not available; however, observed IR and Raman frequencies are in good agreement with those calculated by DFT for a symmetric [4]⁺ structure. Moreover, the lack of coincidences in the IR and Raman spectra† indicates a centrosymmetric, or effectively centrosymmetric, structure for [4]⁺.

The near-IR IVCT bands of of [3]⁺ and [4]⁺, generated by *in situ* chemical oxidation in CH_2Cl_2, are compared in Fig. 2.[9] The solvatochromism of the IVCT band of [4]⁺ (blue shift of 930 cm⁻¹ between CH_2Cl_2 and MeCN) is much closer to that of class-III [1]⁺ cation[4] (blue shift of 860 cm⁻¹) than to that of [3]⁺ (blue shift of 2170 cm⁻¹), suggesting [4]⁺ to be more delocalised than [3]⁺.† Table 1 compares the lineshapes of some IVCT bands.[9] [3]⁺ shows a fairly symmetric band with a bandwidth close to that predicted by Hush theory for a class II system.[10] In contrast, [4]⁺ shows a narrower and less symmetric band, very similar to those of [2a]⁺ and [2b]⁺ (which vibrational data indicate is class III),[5b] supporting assignment to class III. Vibronic coupling simulations of the IVCT of [4]⁺ indicate significant coupling of the electron transfer to symmetric vibrations, as was the case for [2a]⁺.[3a] More evidence for the similarity of [2a]⁺ and [4]⁺ comes from DFT calculations of the reorganisation energies associated with the symmetrical modes; the respective estimates of 1380 and 1490 cm⁻¹ are nearly identical.

The electronic coupling between two redox centers can be evaluated according to the Hush equation:[10]

$$V_H = \mu_{ge}\bar{\nu}_{max}/(eR) \qquad (1)$$

where R is the donor–acceptor separation (diabatic states), e is the electronic charge, and the transition dipole moment, μ_{ge}, of the IVCT band is determined by integration of the band. A problem with using eqn. (1) is in defining the appropriate value of R (*i.e.* in defining the appropriate center of the charge-bearing unit). The values of V_H given in the Table are estimates obtained by equating R to the geometric N–N distances. Whilst these values for [2a]⁺ and [4]⁺ are not directly comparable due to the different media and due to the questionable validity of equating R to the N–N distance, these values do support the idea of comparable delocalisation in the biphenyl and stilbene species, with weaker coupling in the tolane. For class III systems, V is also equal to $\bar{\nu}_{max}/2$; this would

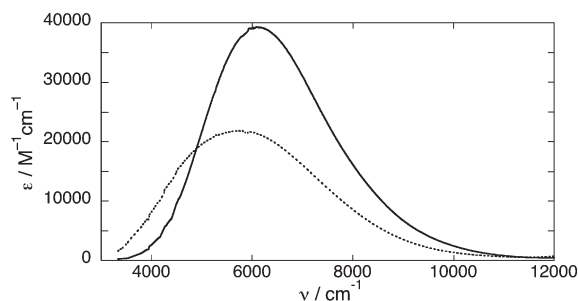**Fig. 2** Intervalence bands of [3]⁺ (broken line) and [4]⁺ (solid line) generated in CH_2Cl_2 by *in situ* oxidation with $[(p\text{-}BrC_6H_4)_3N]^+[SbCl_6]^-$.

Table 1 Energy (cm⁻¹), bandwidth (cm⁻¹) and transition dipole moment (D) for the IVCT for some MV bis(triarylamine) species, with estimated electronic couplings, V, (cm⁻¹; see text for definitions)[a]

	$\bar{\nu}_{max}$	$\bar{\nu}_{1/2}$[b]	$\bar{\nu}_{1/2}$[Hush][c]	Asymmetry[d]	μ_{ge}	V_H	$V_{classIII}$
[2a]⁺ᵉ	6360	3170	3830	1.45	11.6	1550	3180
[3]⁺ᵉ	6190	3960	3780	1.20	11.6[f]	1200[f]	—
[4]⁺	6280	2900	3810	1.34	13.5	1400	3140

[a] All in CH_2Cl_2/0.1 M $[^nBu_4N]^+[PF_6]^-$, apart from μ_{ge} and V_H values for [4]⁺ which are in CH_2Cl_2. [b] Observed width at half-height. [c] Bandwidth according to the relation $\bar{\nu}_{1/2} = \sqrt{(2310\bar{\nu}_{max})}$.[10] [d] Ratio of width on high-energy side to the low-energy side. [e] Data from ref. 2 [f] We find 11.3 D and 1080 cm⁻¹ in CH_2Cl_2.

again indicate very similar degrees of delocalisation in the class-III species [2a]⁺ and [4]⁺ (the discrepancy between V_H and $V_{classIII}$ values indicating that the appropriate value of R is considerably less than the N–N distance). This similarity suggests the effects of a longer N–N separation in [4]⁺ on the electronic coupling are more-or-less compensated by the effects of greater planarity.[11]

The observation of stronger coupling through CH=CH *vs.* C≡C is not unexpected; previous studies have shown this for both inorganic[12] and organic[13] MV systems. However, the current system is unprecedented in that the alkene and alkyne species clearly fall into very different régimes of delocalisation, *i.e.* class III and II, respectively. Moreover, [4]⁺ has the longest bridging group of any class-III bis(triarylamine) studied to date, and allows us to map the class II/III borderline more completely for this type of compound.

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Notes and references

‡ *Crystal data*: for **4** (from hexane): $C_{42}H_{38}N_2O_4$, $M = 634.74$, monoclinic, $a = 10.788(3)$, $b = 12.557(3)$, 12.734(3) Å, $\beta = 105.886(6)°$, $U = 1659.1(7)$ Å³, $T = 120$ K, space group $P2_1/c$, $Z = 2$, μ(Mo–K$_a$) = 0.081 mm⁻¹, 12024 reflections measured, 4027 unique ($R_{int} = 0.0408$), $R(F^2) = 0.0575$ for 1907 data with $I > 2\sigma(I)$, $wR(F^2) = 0.1205$ (all unique data). For [4]⁺[SbF₆]⁻ (from CH_2Cl_2/Et₂O layering): $C_{42}H_{38}F_6N_2O_4Sb$, $M = 870.49$, monoclinic, $a = 10.5478(10)$, $b = 35.449(3)$, 11.1632(11) Å, $\beta = 116.442(2)°$, $U = 3737.3(6)$ Å³, $T = 120$ K, space group $P2_1/n$, $Z = 4$, μ(Mo–K$_a$) = 0.814 mm⁻¹, 43844 reflections measured, 10983 unique ($R_{int} = 0.0329$). $R(F^2) = 0.0613$ for 8265 data with $I > \sigma(I)$, $wR(F^2) = 0.1520$ (all unique data).CCDC reference numbers 252359 and 252360. See http://www.rsc.org/suppdata/cc/b4/b415018j/ for crystallographic data in .cif or other electronic format.

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7 Both DFT and AM1/CI geometry optimisations also suggest **[4]**$^+$ is symmetrical; whilst DFT often leads to overstabilisation of symmetric structures, the AM1/CI results support assignment of **[4]**$^+$ to class III. Moreover, it is important to note that in cases where the MV species has been found to be class III, DFT estimates of the structural and spectroscopic parameters fit very well with experimental data (for example, see refs 4 and 5).

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9 The absorption bands for both **[3]**$^+$ and **[4]**$^+$ are red-shifted in CH$_2$Cl$_2$ relative to CH$_2$Cl$_2$/0.1 M [^{n}Bu$_4$N]$^+$[PF$_6$]$^-$, although this effect is greater for **[3]**$^+$ (red shift of 430 cm^{-1}) than **[4]**$^+$ (200 cm^{-1}); however, the band shapes are only slightly affected by the presence or absence of electrolyte. Also note that spectra of **[4]**$^+$[SbF$_6$]$^-$ are essentially identical to spectra generated by *in situ* oxidation of neutral **4**.

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11 For class-II MV species, either the stilbene- or biphenyl-like example may show the stronger coupling depending on the system in question (*e.g.* refs 12 and 13).

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