

SUPPORTING INFORMATION FOR

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

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Synthetic Procedures

General. Electrochemical measurements were carried out under argon on dry deoxygenated dichloromethane solutions ca. 10^{-4} M in analyte and 0.1 M in tetra-*n*-butylammonium hexafluorophosphate using a BAS Potentiostat, a glassy carbon working electrode, a platinum auxiliary electrode, and, as a pseudo-reference electrode, a silver wire anodized in 1 M aqueous potassium chloride. Potentials were referenced to ferrocenium / ferrocene by using cobaltocenium hexafluorophosphate¹ as an internal reference (since many of the redox events of interest were at similar potentials to that of ferrocene). Cyclic voltammograms were recorded at a scan rate of 50 mVs⁻¹; differential pulse voltammograms were run at 20 mVs⁻¹, with a pulse height of 50 mV, on the same sample, to afford better resolution of the overlapping peaks. FT-IR data were recorded on a Perkin-Elmer Spectrum 1000 spectrometer using pressed KBr pellets for [4]⁺[SbF₆]⁻, whilst [3]⁺ solutions were studied in CH₂Cl₂. Raman data were acquired on solid samples diluted and ground with KBr, and in dichloromethane solution, using a Bruker FRA106/S module attached to a Equinox 55 FT-IR spectrometer, utilizing a laser with $\lambda = 1064$ nm (hence there is likely to be some resonant enhancement for spectra of [4]⁺[SbF₆]⁻). X-band EPR spectra were acquired using a Bruker EMX spectrometer. UV-vis.-NIR spectra were recorded in 1 cm cells using a Varian Cary 5E spectrometer. **3** was synthesized according to the literature procedure.² The [3]⁺ and [4]⁺ cations were generated in solution by addition of a solution of tris(4-bromophenyl)aminium hexafluoroantimonate (Aldrich) in dry solvent to a solution of an excess of the appropriate neutral amine.

***E*-4,4'-Dibromostilbene.** *E*-4,4'-Dibromostilbene was prepared from diethyl 4-bromobenzylphosphonate and 4-bromobenzaldehyde using phase-transfer conditions analogous to those described by Piechucki.³ 50% aqueous sodium hydroxide (20 mL) was added to a solution of diethyl 4-bromobenzylphosphonate (5.66 g, 18.4 mmol) and 4-bromobenzaldehyde (3.41 g, 18.4 mmol) in benzene (20 mL). Tetra-*n*-butylammonium iodide (420 mg) was added and the mixture was refluxed under nitrogen for 30 minutes. The reaction mixture was allowed to cool and diluted by the addition of water (50 mL). The white solids were collected on a frit and washed with methanol and diethyl ether before drying *in vacuo* (3.39 g, 10.0 mmol, 55%); NMR data were in agreement with published data.⁴

***E*-4,4'-Bis[4-bis(4-methoxyphenyl)amino]stilbene, 4.** Bis(4-methoxyphenyl)amine^{5,6} (1.85 g, 8.07 mmol) and *E*-4,4'-dibromostilbene (1.36 g, 4.03 mmol) were dissolved in toluene (20 mL) under nitrogen and sodium *tert*-butoxide (1.55 g, 16.14 mmol),

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tris(bezylideneacetone)dipalladium (0.111 g, 0.121 mmol), and 1,1'-bis(diphenylphosphino)ferrocene (0.134 g, 0.242 mmol) were added. The reaction mixture was heated to 110 °C for 15 h, allowed to cool to room temperature and partitioned between water and dichloromethane. The aqueous layer was extracted with additional dichloromethane and the combined organic layers were dried on MgSO₄, filtered, and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, 4:1 hexane / dichloromethane), followed by recrystallization from hexanes to give yellow blades (2.00 g, 3.15 mmol, 78%). ¹H NMR (acetone-*d*₆, 300 MHz) δ 7.36 (d, *J* = 8.6 Hz, 4H), 7.04 (d, *J* = 9.0 Hz, 8H), 6.99 (s, 2H), 6.89 (d, *J* = 9.0 Hz, 8H), 6.81 (d, *J* = 8.6 Hz, 4H), 3.79 (s, 12 H). ¹H NMR (benzene-*d*₆, 300 MHz) δ 7.29 (d, *J* = 8.8 Hz, 4H), 7.07 (apparent d, *J*_{app} = 9.0 Hz, 12H), 6.98 (s, 2H), 6.69 (d, *J* = 9.0 Hz, 8H), 3.32 (s, 12H). ¹³C{¹H} NMR (benzene-*d*₆, 75 MHz) δ 156.4 (quat.), 148.4 (quat.), 141.4 (quat.), 131.0 (quat.), 127.6 (CH), 126.8 (CH), 126.5 (CH), 121.4 (CH), 115.2 (CH), 55.2 (CH₃). IR (KBr) ν 1602, 1504, 1460, 1438, 1324, 1282, 1242, 1178, 1112, 1102, 1029, 971, 825, 782, 728, 714, 649, 640, 629, 575, 538, 519 cm⁻¹. Raman (KBr) ν 1625, 1594, 1556, 1427, 1330, 1311, 1196, 11278, 1164 cm⁻¹. Anal. Calcd. for C₄₂H₃₈N₂O₄: C, 79.47; H, 6.03; N, 4.41. Found: C, 79.07; H, 5.96; N, 4.27. EI HRMS calcd for C₄₂H₃₈N₂O₄: 634.2832. Found: 634.2862.

Hexfluoroantimonate Salt of *E*-4,4'-Bis[4-bis(4-methoxyphenyl)amino]stilbene, [4]⁺[SbF₆]⁻. A solution of AgSbF₆ (3 mL, containing 62 mg, 0.11 mmol AgSbF₆) in dry dichloromethane was added to **4** (86 mg, 0.14 mmol) under nitrogen. After 30 min, the blue solution was diluted with more dry dichloromethane (3 mL), filtered into an ampoule using a syringe filter (0.2 μm) to remove silver metal, and layered with dry diethyl ether (25 mL). After 1 week, the resulting green-gold blade-like crystals of [4]⁺[SbF₆]⁻ (69 mg, 0.079 mmol, 72%) were isolated by removal of the supernatant by cannula, washing with dry diethyl ether (4 × 10 mL), and drying in vacuo. Anal. Calcd. for CHNOSb: C, 57.95; H, 4.40; N, 3.22. Found: C, 57.65; H, 4.16; N, 3.17. IR (KBr) ν 1604, 1589, 1542, 1500, 1462, 1436, 1358, 1298, 1244, 1187, 1153, 1109, 1029, 1007, 830, 814, 795, 659, 639, 572 cm⁻¹. Raman (KBr) ν 1593, 1554, 1488, 1453, 1327, 1284, 1193, 1171 cm⁻¹. Raman (CH₂Cl₂) ν 1604, 1554, 1327, 1284, 1169 cm⁻¹.

Computational Details. Geometry optimizations of the neutral **4** and its radical-cation, [4]⁺, were performed at both the semi-empirical Hartree-Fock Austin Model 1 (AM1) and Density Functional Theory (DFT) levels. The correlated AM1-HF (AM1/CI) scheme, within a limited active space, was also utilized for investigation of the of radical-cation electronic states. The DFT calculations were carried-out using the B3LYP functional, where Becke's three-parameter hybrid exchange functional⁷ is combined with the Lee-Yang-Parr correlation functional,⁸ with a 6-31G* split valence plus polarization basis set. IR and Raman frequency analyses were performed at the DFT level; a scaling factor of 0.9613 was utilized for alignment of the theoretical bands with the experimental measurements. DFT calculations of the reorganization energies associated with the coupling of symmetrical modes to the IVCT of [4]⁺ were performed as previously described.⁹ All AM1-based methods were carried-out using the implementation in the AMPAC¹⁰ software package, while the DFT calculations were performed with Gaussian98.¹¹ Vibronic coupling simulation of the spectral lineshape of the IVCT of [4]⁺ was performed as previously described.⁹

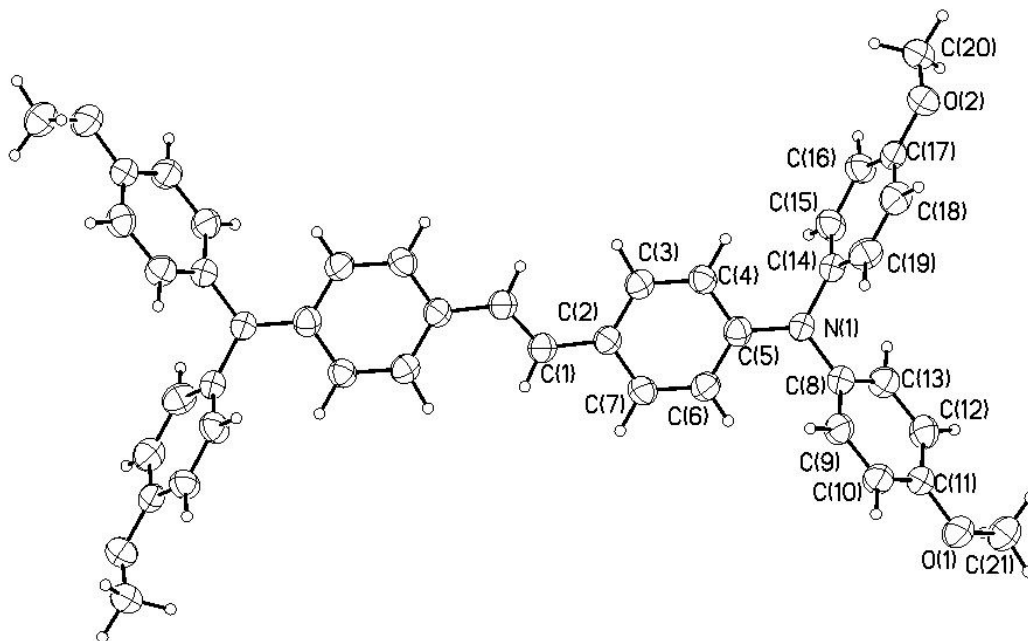


Figure S1. View of the molecular structure of **4** from its crystal structure showing the atomic labelling scheme. The molecule sits on a crystallographic inversion centre.

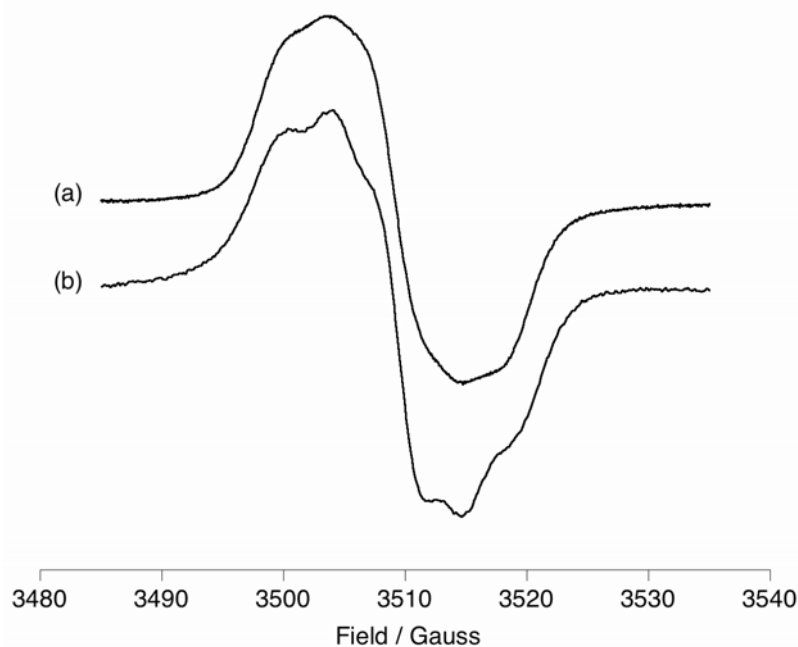


Figure S2. First-derivative room-temperature EPR spectra of (a) a CH_2Cl_2 solution of crystalline $[\mathbf{4}]^+[\text{SbF}_6]^-$ and (b) a CH_2Cl_2 solution of $[\mathbf{3}]^+[\text{SbCl}_6]^-$ generated in situ using tris(4-bromophenyl)ammonium hexafluoroantimonate. Both spectra can be modelled as five-line spectra arising from poorly resolved coupling to two equivalent $I = 1$ nitrogen centers. In both cases, $g = 2.004$ and $A_N = \text{ca. } 4.3 \text{ G}$.¹²

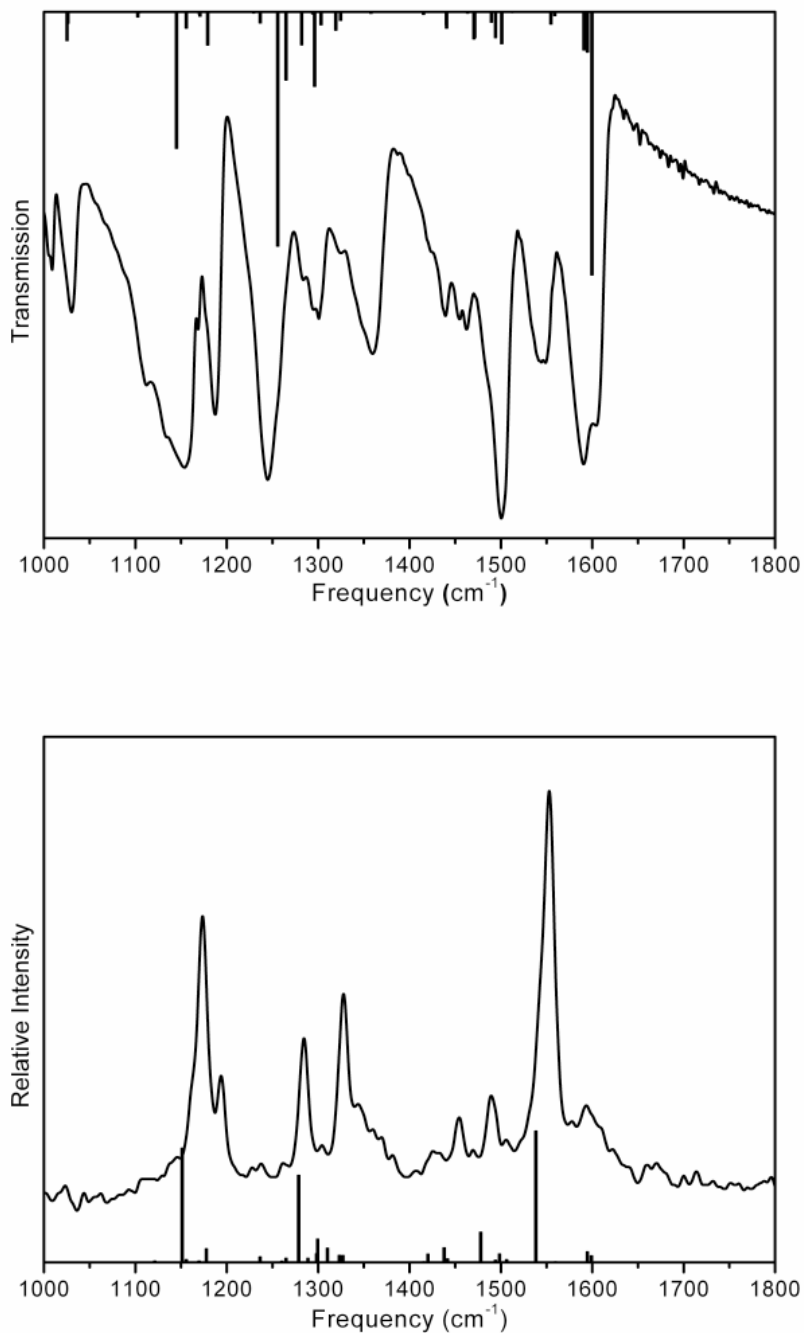


Figure S3. Experimental IR (above) and Raman (below) spectra of $[4]^+[\text{SbF}_6]^-$ (KBr) compared to DFT-calculated spectra for the $[4]^+$ cation. Raman spectra in dichloromethane are also similar, but suffer more complications from absorption.

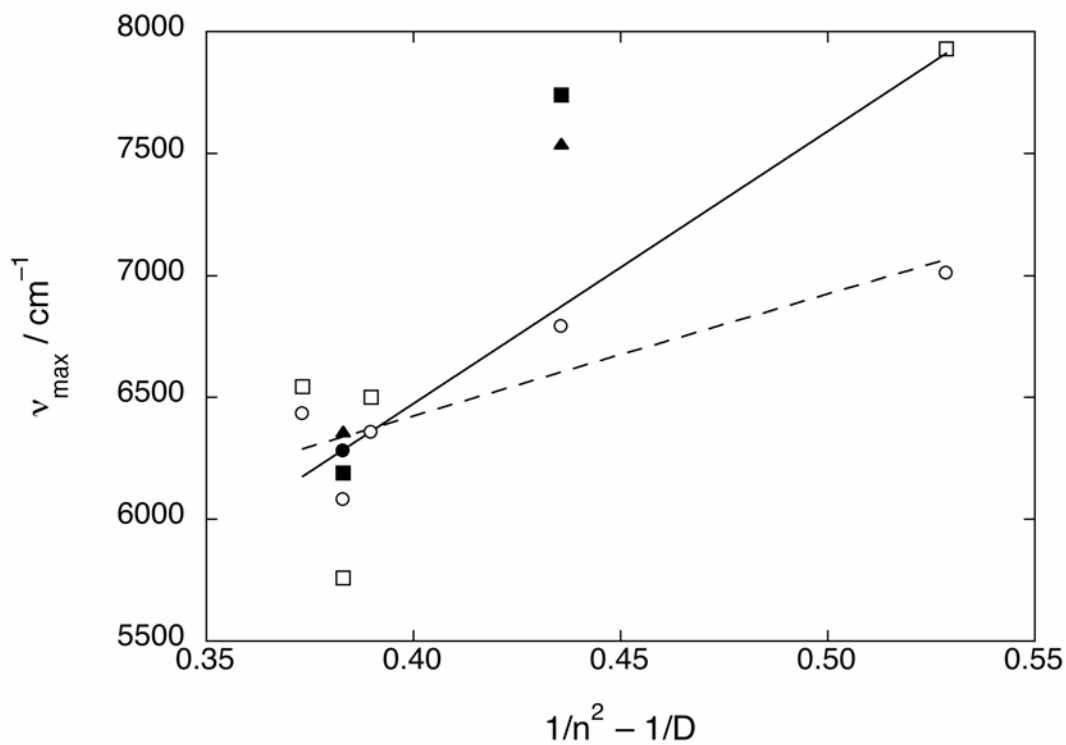


Figure S4. Comparison of the solvatochromism of the IVCT absorption of **[2a]⁺** (triangles), **[3]⁺** (squares), and **[4]⁺** (circles). Open symbols represent data acquired by chemical oxidation in the pure solvent; closed symbols represent data acquired in 0.1 M $[\text{tBu}_4\text{N}]^+[\text{PF}_6]^-$, either using chemical oxidation (**[3]⁺**) or electrochemical oxidation (**[2a]⁺** and **[3]⁺**, data from reference 2), and are plotted against the polarity of the solvent used with no attempt to correct for the presence of the electrolyte. The solid and broken lines represent least-squares fits to the data recorded in electrolyte-free solvent for **[3]⁺** and **[4]⁺** respectively. The solvents, in order of increasing $(1/n^2 - 1/D)$, are THF, CH_2Cl_2 , PhCN, DMSO and MeCN.

References

- (1) Using a value of $E_{1/2}$ for the cobaltocenium / cobaltocene couple of -1320 mV vs. ferrocenium / ferrocene in dichloromethane (S. Barlow, *Inorg. Chem.*, 2001, **40**, 7047).
- (2) C. Lambert and G. Nöll, *J. Am. Chem. Soc.*, 1999, **121**, 8434.
- (3) C. Piechucki, *Synthesis*, 1976, 187.
- (4) M. Baumgarten and T. Yuksel, *Phys. Chem. Chem. Phys.*, 1999, **1**, 1699.
- (5) H. Zhao, C. Tanjutco, and S. Thayumanavan, *Tetrahedron Lett.*, 2001, **42**, 4421.
- (6) J. M. Kauffman and G. Moyna, *J. Org. Chem.*, 2003, **68**, 839.
- (7) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
- (8) C. T. Lee, W. T. Yang, and R. G. Parr, *Phys. Rev.*, 1988, **B37**, 785.
- (9) V. Coropceanu, M. Malagoli, J. M. André, and J. L. Brédas, *J. Am. Chem. Soc.*, 2002, **124**, 10519.
- (10) *AMPAC 6.55 User's Manual.*, Semichem: 7128 Summit, Shawnee, KS 66216, 1997.
- (11) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. Montgomery, J.A., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, P. Salvador, J. J. Dannenberg, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, *Gaussian98, Rev. A.11*, 1998.
- (12) For comparison, the ^{14}N coupling constant, A_{N} , in the tris(*p*-anisyl)aminium radical cation is 8.97 G in MeCN (E. T. Seo, R. F. Nelson, J. M. Fritsch, L. S. Marcoux, D. W. Leedy, and R. N. Adams, *J. Am. Chem. Soc.*, 1966, **88**, 3498). Whilst the ESR spectra of several tris(aryl)aminium radical cations, such as the tris(*p*-anisyl)aminium cation, also show very well-resolved ^1H coupling, the lack of such resolution in the present cases is not particularly surprising given the number of inequivalent protons; for example, the tris(biphenyl-4-yl)aminium cation shows a poorly resolved spectrum that has been attributed to the large number of inequivalent protons (G. A. Pearson, M. Rocek, and R. I. Walter, *J. Phys. Chem.*, 1978, **82**, 1185).