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Molecular rectification: dipole reversal in a cationic donor–(π-bridge)–acceptor dye

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The cationic donor–(π-bridge)–acceptor dye, *E*-4-[(*N*-alkyl-5,6,7,8-tetrahydroisoquinolinium-5-ylidene)methyl]-*N*,*N*-dibutylaniline octadecyl sulfate is a molecular rectifier. Its Langmuir–Blodgett films exhibit asymmetric current–voltage characteristics but the dodecyl and octadecyl analogues behave differently. Rectification occurs in opposite quadrants of the *I*–*V* plot as a consequence of anion-induced dipole reversal: the aromatic form ($D{-}\pi{-}A^+{-}C_nH_{2n+1}$) exists when the negatively charged sulfate is adjacent to the heterocycle and the quinonoid form ($D^+{=}\pi{=}A'{-}C_nH_{2n+1}$ where A′ is the donor) when it is adjacent to the amino group. This is supported by the fact that mixed monolayers of the two dyes do not exhibit second-harmonic generation whereas films of the individual dyes have high second-order susceptibilities (*e.g.* $\chi^{(2)}_{zzz} = 100$ pm V^{-1} at 1.064 μm for the dodecyl analogue). The monolayer structure is non-centrosymmetric and, therefore, the nonlinear optical behaviour can only be interpreted as above. Theoretical modelling has also verified the transition as the counterion is relocated. MNDO, AM1 and PM3 calculations indicate changes of *ca.* 0.08 Å in the C–C bonds of the central bridging unit as well as the exocyclic C–N bond. It is the first time that anion-induced dipole reversal has been observed.

Introduction

Molecules that comprise donor and acceptor groups, linked *via* an electron bridge, may be classified as organic counterparts of the pn junction.[1] However, difficulties of alignment and experimental verification have resulted in reports of molecular rectification from only three examples to date: a zwitterionic molecule[2–4] and cationic dye,[5] both of which are π-bridged but by necessity have non-planar structures to suppress resonance between the charge-transfer states, and a donor–(σ-bridge)–acceptor molecule.[6] The first and most extensively studied of these, *Z*-β-(*N*-hexadecylquinolinium-4-yl)-α-cyano-4-styryldicyanomethanide, was synthesised as part of Cranfield's nonlinear optics programme.[7] It has since been the subject of several theoretical investigations[8–10] and found to exhibit asymmetric current–voltage characteristics, albeit using oxidisable electrodes.[2,3] Early studies restricted the top electrode to metals with low sublimation temperatures to avoid shorting through the fragile organic film. However, an unambiguous assignment of molecular rectification has been obtained by sandwiching both the monolayer and multilayer films between gold.[4]

A fourth example, the dodecyl analogue of the cationic dye shown in Fig. 1, is reported in this work and the rectifying behaviour compared with that of the previously studied octadecyl analogue.[5] We demonstrate for the first time that the molecular dipole is influenced by electrostatic polarization, reversing from $D{-}\pi{-}A^+$ to $D^+{=}\pi{=}A'$ as the negatively charged counterion is relocated to the opposite end of the chromophore. This is manifested by the rectification occurring in different quadrants of the current–voltage plots and verified by a quenching of the second-harmonic intensity from mixed monolayers of the two forms. Theoretical calculations demonstrate a dependence of the molecular dimensions on the location of the counterion. They corroborate dipole reversal and confirm the transition from an aromatic to quinonoid form.

Experimental

To a solution of *N*-dodecyl-5,6,7,8-tetrahydroisoquinolinium iodide (0.43 g, 1 mmol) and *N*,*N*-dibutylaminobenzaldehyde (0.23 g, 1 mmol) in methanol (20 cm^3) was added piperidine (0.1 cm^3) and the resultant mixture was heated at reflux for 12 h. Upon cooling, red microcrystals of the iodide salt of *E*-4-[(*N*-dodecyl-5,6,7,8-tetrahydroisoquinolinium-5-ylidene)methyl]-*N*,*N*-dibutylaniline were collected and recrystallised from methanol: yield 40%; mp 165–166 °C. Found: C, 66.89; H, 8.87; N, 4.33%. $C_{36}H_{57}N_2I$ requires: C, 67.06; H, 8.91; N, 4.34%. ^{1}H NMR ($CDCl_3$, 250 MHz, *J*/Hz): δ_H 0.88 (t, *J* 6.4, 3H, CH_3), 0.98 (t, *J* 7.2, 6H, CH_3), 1.25 (br s, 18H, CH_2), 1.37 (q, *J* 7.4, 4H, CH_2), 1.55–1.64 (m, 4H, CH_2), 1.91–1.99 (m, 4H, CH_2), 2.92–2.99 (m, 4H, C=C-CH_2), 3.34 (t, *J* 7.6, 4H, CH_2N),

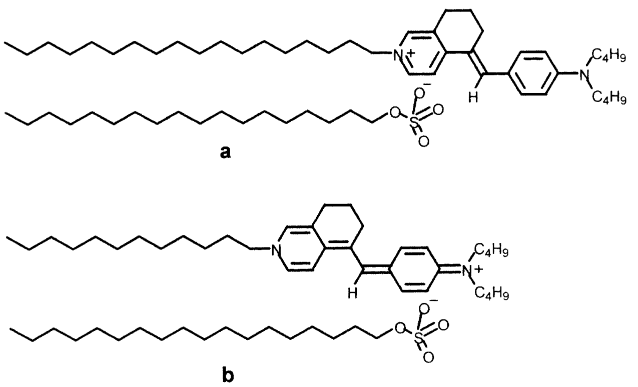

Fig. 1 Molecular structures of *E*-4-[(*N*-alkyl-5,6,7,8-tetrahydroisoquinolinium-5-ylidene)methyl]-*N*,*N*-dibutylaniline octadecyl sulfate schematically showing the lengths of the dodecyl and octadecyl analogues relative to the octadecyl sulfate counterion. Theoretical modelling corroborates a change in the bond alternation, from an aromatic to quinonoid form, as the negatively charged sulfate relocates from the isoquinolinium towards the amino group

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4.64 (t, *J* 7.2, 2H, CH_2N^+), 6.67 (d, *J* 8.6, 2H, Ar-H), 7.45 (d, *J* 8.5, 2H, Ar-H), 7.46 (s, 1H, C=C-H), 8.06 (d, *J* 6.7, 1H, Qn-H), 8.65 (d, *J* 6.5, 1H, Qn-H), 8.77 (s, 1H, Qn-H). *m/z* (FAB): 517 $[M - I^-]^+$.

The iodide salt of the dye (in chloroform) and sodium octadecyl sulfate (in methanol) were spread, in a 1 : 1 mole ratio, onto the pure water subphase of a Langmuir–Blodgett (LB) trough. The Na^+ and I^- ions dissolve, leaving the amphiphilic species at the air–water interface which form an organised monolayer when compressed at 0.5 $cm^2\ s^{-1}$. The floating monolayer was deposited on the upstroke at a surface pressure of 30 mN m^{-1} and a rate of 5 mm min^{-1}. Films of the octadecyl analogue were fabricated in a similar manner. Mixed films of the dodecyl and octadecyl analogues, in a 1 : 1 ratio, were also obtained with either one or both of the iodide counterions replaced by octadecyl sulfate.

Pressure–area isotherms of the individual dyes exhibit three distinct features: a low-pressure regime where the hydrophilic chromophore is initially parallel to the surface, this being separated by a broad plateau from a steep high-pressure regime where the molecules are upright (Fig. 2). Films deposited onto 10 MHz quartz crystals from the high-pressure regime, *i.e.* at a surface pressure of 30 mN m^{-1}, have a footprint of 0.45 ± 0.04 nm^2 $molecule^{-1}$ in contact with substrate, the value being consistent for both analogues and obtained from a Sauerbrey analysis[11] of the frequency change. This area corresponds to the sum of the molecular cross-sections of the amphiphilic dye and amphiphilic counterion, which pack side-by-side.

The pressure–area isotherm of a mixed film of the two analogues, with both counterions exchanged, indicates phase separation. The transitions mimic those of the individual components, albeit with a 2 mN m^{-1} increase in surface pressure and areas modified by the presence of the second dye (Fig. 2). By comparison with the individual isotherms, the dodecyl and octadecyl analogues undergo transitions at *ca.* 18 and 27 mN m^{-1} respectively in the mixed film. In contrast, a mixed anion salt, obtained by spreading solutions of the iodide salts of the dodecyl and octadecyl analogues in a 1 : 1 : 1 ratio with sodium octadecyl sulfate, is distinctive and displays a single transition (Fig. 3). There is no phase separation and the properties of the mixed monolayer, referred to below, correspond to this mixed anion combination.

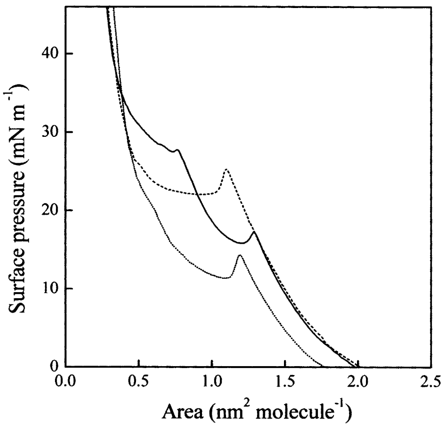


Fig. 2 Surface pressure *versus* area isotherms: *E*-4-[(*N*-dodecyl-5,6,7,8-tetrahydroisoquinolinium-5-ylidene)methyl]-*N*,*N*-dibutylaniline iodide and sodium octadecyl sulfate co-spread in a 1 : 1 mole ratio at the air–water interface (lower dotted line); corresponding data for the octadecyl analogue (upper broken line); a mixed film where the iodide salts of both analogues are co-spread in a 1 : 1 : 2 ratio with sodium octadecyl sulfate (solid line). The water-soluble anions, Na^+ and I^-, dissolve in the subphase and are not incorporated into the film.

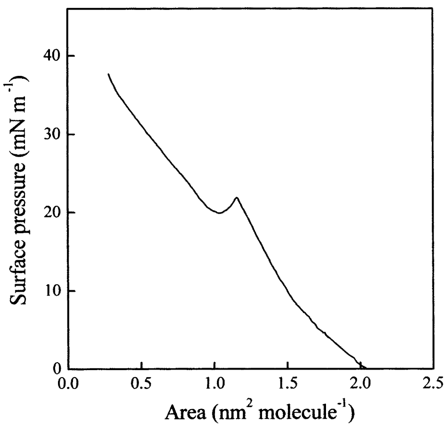


Fig. 3 Surface pressure *versus* area isotherm of a mixed film where the iodide salts of the dodecyl and octadecyl analogues are co-spread in a 1 : 1 : 1 ratio with sodium octadecyl sulfate. There is no evidence of the phase separation as indicated by films obtained using a 1 : 1 : 2 ratio.

Results and discussion

Molecular alignment

Multilayer films of amphiphilic materials tend to be centric with the hydrophobic tails aligned at one interface and the hydrophilic components at the next.[12,13] However, in this case, a non-centrosymmetric packing arrangement is stabilised by the upper and lower surfaces of the individual layers, which are sufficiently hydrophobic to suppress realignment. This has been confirmed by second-harmonic generation studies both for films deposited on glass and those prepared for rectification studies. As is common for most LB films, the second-harmonic intensity is negligible at normal incidence (Fig. 4a) indicating that the intramolecular charge-transfer axis is inclined towards the vertical rather than the horizontal. There is also a strong polarization dependence, *e.g.* $I^{2\omega}(p \rightarrow p)/I^{2\omega}(s \rightarrow p) \approx 12$ for films of the dodecyl analogue when the laser beam (Nd : YAG) is incident at 45° to the film. Using the analysis of Kajikawa *et al.*,[14] this relates to a chromophore tilt angle of 36° from the normal and may be compared with the corresponding value of 33° for the octadecyl analogue.

The second-harmonic intensity increases quadratically with the film thickness, to more than 100 layers, indicating non-centrosymmetric alignment and long-range structural order (Fig. 4b). The films are almost transparent at the harmonic wavelength and, thus, it may be assumed that Kleinman's symmetry is valid and that the components of the second-order susceptibility are limited to $\chi^{(2)}_{zzz}$ and $\chi^{(2)}_{zxx}$. By reference to the Maker fringe envelope of a Y-cut quartz reference (d_{11} = 0.5 pm V^{-1}), susceptibilities of $\chi^{(2)}_{zzz} = 100$ and $\chi^{(2)}_{zxx} = 26$ pm V^{-1} at $\lambda = 1.064$ μm have been obtained for the dodecyl analogue. These correspond to a molecular hyperpolarizability (β) of 8.5×10^{-38} $m^4\ V^{-1}$. The values were calculated for a thickness of 2.8 nm $layer^{-1}$ and refractive indices of $n^{2\omega} = 1.58$ and $n^{\omega} = 1.52$, obtained by analysis of the angular dependence of the polarized reflectance. Importantly, the LB film has a peak absorbance at 410 nm with cut-off above *ca.* 700 nm (Fig. 5). The absorbance diminishes to only 7×10^{-4} $layer^{-1}$ at 532 nm and thus, for second-harmonic generation, there is an optimal trade-off in the transparency and resonantly enhanced efficiency at the harmonic wavelength.

The corresponding data for the octadecyl analogue have been reported.[15] Its multilayers exhibit lower susceptibilities of $\chi^{(2)}_{zzz} = 30$ pm V^{-1} and $\chi^{(2)}_{zxx} = 5$ pm V^{-1} at 1.064 μm and have a peak absorbance at 430 nm. However, the values are improved to 76 and 16 pm V^{-1} respectively when the dye is co-deposited in a 1 : 1 ratio with octadecanoic acid, as mixed monolayers, and then fabricated as a multilayer. This may be attributed to resonant enhancement as the peak absorbance is

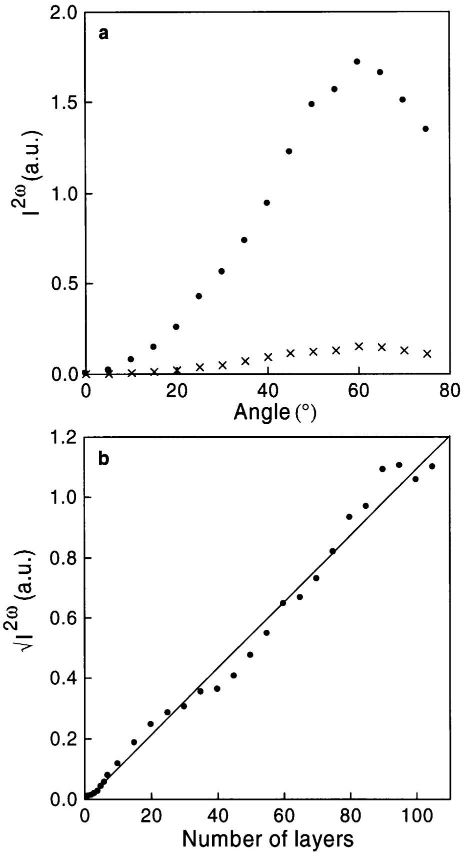


Fig. 4 Nonlinear optical properties of *E*-4-[(*N*-dodecyl-5,6,7,8-tetrahydroisoquinolinium-5-ylidene)methyl]-*N*,*N*-dibutylaniline octadecyl sulfate: (a) second-harmonic intensity *versus* the angle of incidence of the Nd : YAG laser beam relative to the LB film for s-polarized (x) and p-polarized (solid circles) light; (b) variation of the square root of the second-harmonic intensity with the number of layers for the p-polarized beam incident at 45° the film.

red shifted to 450 nm, *i.e.* towards the harmonic wavelength. However, it may also relate to improved non-centrosymmetric ordering or, as reported by Hayden[16] and McGilp *et al.*[17] for related dyes, to changes in the local field effects. In contrast, LB films of the dodecyl analogue, reported in this work, exhibit a reduced second-harmonic intensity when diluted.

Rectification and dipole reversal

The nonlinear optical data have been presented here to demonstrate that the film structure is non-centrosymmetric. It is one of few materials to pack in this manner with most adopting centric head-to-head (hydrophilic) and tail-to-tail (hydrophobic) arrangements at successive interfaces. It provides an opportunity to compare the rectifying behaviour with that of the previously reported octadecyl analogue,[5] where dissimilar lengths of the amphiphilic dye and amphiphilic counterion probably result in a slightly different packing arrangement. At the air–water interface, the isoquinolinium ring of the octadecyl substituted analogue locates next to the negatively charged sulfate group as a consequence of the hydrophilic nature of the head groups and van der Waals interactions between hydrophobic tails of equal length. However, for the shorter dodecyl analogue, reported in this work, the sulfate group is closer to the amino group because the molecular lengths rather than the lengths of their tails are similar: *ca.* 3.3 nm for the dye and 2.9 nm for the counterion.

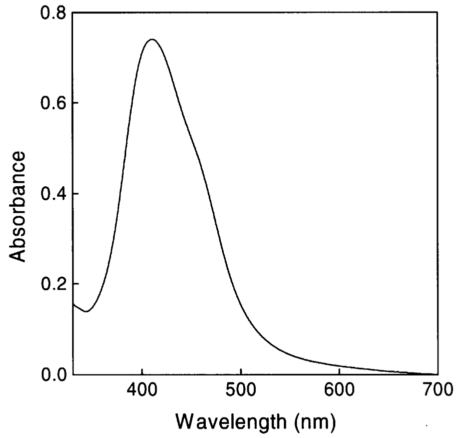


Fig. 5 UV/visible spectrum of a 105 layer film of *E*-4-[(*N*-dodecyl-5,6,7,8-tetrahydroisoquinolinium-5-ylidene)methyl]-*N*,*N*-dibutylaniline octadecyl sulfate. The asymmetric peak may be resolved into two symmetrical bands centred about 405 and 450 nm.

This paper focuses upon molecular rectification from multilayer films and, in particular, on the profound effect of the location of the anion on the rectifying behaviour of the cationic dye sandwiched between symmetrical electrodes: gold or aluminium. Films were deposited to *ca.* forty layers onto rectangular glass substrates, coated at one end with a 10 nm thick electrode to permit second-harmonic generation studies to be performed at the other. This provided confirmation of optimum alignment. Gold or aluminium pads, with a diameter of 1 mm, were thermally evaporated onto the LB film, again to a thickness of 10 nm, using an Edwards 306 coating unit. This was performed at 10^{-4} Pa with a deposition rate of 0.1 nm s^{-1} and a distance of 0.2 m between the source and substrate.

The current–voltage characteristics are asymmetric (Fig. 6) and, with non-oxidisable noble metal electrodes, the behaviour

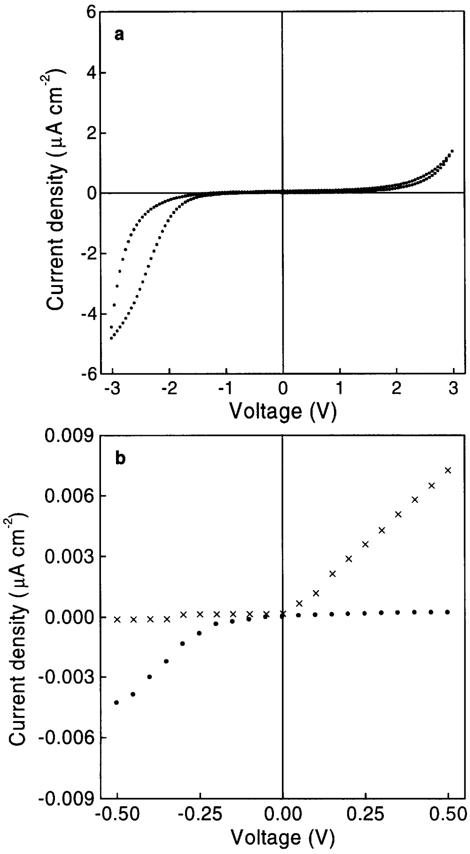


Fig. 6 Current–voltage characteristics: (a) a multilayer film of the dodecyl analogue cycled between +3 and −3 V; (b) films of the dodecyl and octadecyl analogues in the +0.5 to −0.5 V range which rectify in the positive and negative quadrants respectively. Similar data have been obtained for gold/(LB film)/gold and aluminium/(LB film)/aluminium structures and, in each case, the required polarity for rectification is as shown.

may be unambiguously assigned to rectification by the molecular layer. With an appropriate bias, electrons tunnel from the electrode to the adjacent acceptor and, at the other end of the device, from the donor to the second electrode. Electron tunnelling in the opposite direction, between the electrodes and dye under reverse bias, is not readily achievable because the donor is a poor electron-acceptor and the acceptor a poor electron-donor. Rectification is reproducible for both the gold and aluminium electrode configurations but the required polarity is different for the two analogues. This is clearly demonstrated in Fig. 6b where the current–voltage curves are similar but rectification occurs in opposite quadrants of the current–voltage plots: at $-I/-V$ for the octadecyl analogue and $+I/+V$ for the dodecyl analogue. It implies that the molecular dipoles are reversed although, from the initial alignment at the air–water interface and deposition on the upstroke only, the molecular orientation should be consistent. Therefore, we suggest that the dipole is independent of the molecular orientation and that the reversal may be explained by an altered location of the negatively charged counterion, relative to the donor and acceptor groups, which induces a change in the charge-transfer state (Fig. 1). This may also explain hysteresis of the current–voltage characteristics, shown in Fig. 6a, which probably results from field-induced shifts of the counterion relative to the active donor and acceptor groups.

SHG cancellation in mixed monolayers

Experimental evidence of dipole reversal is also provided by changes in the second-harmonic intensity of both alternate-layer and mixed monolayer films. It is partially cancelled when a monolayer of the dodecyl analogue is deposited onto a monolayer of the octadecyl analogue, and *vice versa*. Furthermore, in the absence of phase separation, it is totally quenched when the dyes are co-deposited in a 1 : 1 ratio as a mixed monolayer. Following alignment at the air–water interface, the monolayer structure is non-centrosymmetric and, thus, quenching can only be explained if the molecular dipoles are opposed. This is simply achieved by the negatively charged ions being adjacent to the amino group in one analogue and the isoquinolinium group in the other, with a net cancellation of the molecular dipoles when the dyes are mixed in an appropriate 1 : 1 ratio.

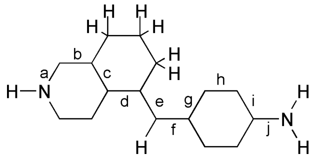
Theoretical analysis

The hypothesis of anion-induced dipole reversal has also been verified by theoretically modelling a simplified molecule, where the anion is $CH_3OSO_3^-$ and either H or CH_3 replaces the alkyl groups of the dye (Tables 1 and 2). Using the MOPAC programme of Cerius2 (Accelrys, Cambridge), MNDO, AM1 and PM3 calculations corroborate reversal and demonstrate a dependence of the molecular dimensions on the location of a probe charge. They show a transition from the expected aromatic structure of the dye to the quinonoid form, normally attributed to the excited state for the isolated molecule, as the counterion is moved from the isoquinolinium end towards the amino group. Differences in the dimensions of the two forms are very pronounced for the exocyclic carbon–nitrogen bond of the amino group (*ca.* 0.08 Å) as well as the central bridging unit (*ca.* 0.08 Å), whose lengths are susceptible to change and exhibit strong bond alternation. Furthermore, when $CH_3CO_2^-$ is used as the counterion, the theoretical minimisation results in closer intermolecular contacts and differences of >0.1 Å in the bond lengths of the central bridging units of the two forms: *e.g.* 1.502 (single), 1.361 (double) and 1.478 (single) Å for the aromatic form and 1.377, 1.473 and 1.370 Å for the quinonoid form. However, when the probe charge is located towards the centre of the molecular unit, the dimensions are intermediate of the above and show no alternation.

Conclusion

Anion-induced dipole reversal has been demonstrated by an altered polarity for rectification, suppression of the second-harmonic intensity from a non-centrosymmetric monolayer of the two analogues and, in addition, theoretical modelling. It is the first example of such behaviour and provides an alternative explanation of previously reported nonlinear optical data of LB films of related cationic dyes: for example, signal instability in many cases; vastly different anion-dependent susceptibilities of 80 to 1500 pm V^{-1} for films of the same chromophore;[18] a greatly improved susceptibility when electrically poled even though the amphiphilic dye is aligned at the air–water interface prior to deposition.[19] These anomalies probably relate to the location of the anions, which is probably variable for spherical species, and the behaviour should be improved by considering the structure of the counterion as well as the optically nonlinear

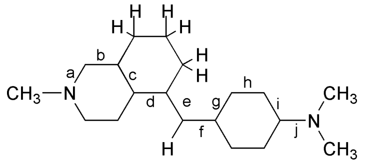
Table 1 Theoretically modelled bond lengths of a simplified dye, *E*-4-[(5,6,7,8-tetrahydroisoquinolinium-5-ylidene)methyl]aniline methyl sulfate, from MNDO, AM1 and PM3 calculations; the aromatic and quinonoid forms relate to molecular structures with the negatively charged counterion located at the isoquinolinium and anilinium ends respectively



	Aromatic form			Quinonoid form			
Bond[a]	MNDO	AM1	PM3	MNDO	AM1	PM3	Difference Δ(Ar − Q)
a/Å	1.374	1.359	1.366	1.391	1.379	1.396	−0.022
b/Å	1.404	1.401	1.393	1.380	1.372	1.363	+0.028
c/Å	1.429	1.411	1.405	1.468	1.447	1.444	−0.038
d/Å	1.485	1.461	1.468	1.406	1.378	1.385	+0.082
e/Å	1.364	1.352	1.346	1.446	1.428	1.427	−0.080
f/Å	1.479	1.453	1.460	1.396	1.372	1.371	+0.084
g/Å	1.414	1.403	1.397	1.459	1.443	1.443	−0.044
h/Å	1.402	1.389	1.388	1.372	1.357	1.351	+0.033
i/Å	1.420	1.418	1.404	1.455	1.454	1.450	−0.039
j/Å	1.417	1.392	1.425	1.352	1.323	1.325	+0.078

[a] The bond lengths for the rings each correspond to the mean of the two related dimensions.

Table 2 Theoretically modelled bond lengths of a simplified dye, *E*-4-[(*N*-methyl-5,6,7,8-tetrahydroisoquinolinium-5-ylidene)methyl]-*N*,*N*-dimethylaniline methyl sulfate, from MNDO, AM1 and PM3 calculations; the aromatic and quinonoid forms relate to molecular structures with the negatively charged counterion located at the isoquinolinium and anilinium ends respectively



Bond[a]	Aromatic form MNDO	AM1	PM3	Quinonoid form MNDO	AM1	PM3	Difference Δ(Ar − Q)
a/Å	1.383	1.369	1.373	1.403	1.385	1.396	−0.020
b/Å	1.404	1.400	1.393	1.374	1.370	1.361	+0.031
c/Å	1.426	1.410	1.405	1.467	1.446	1.442	−0.038
d/Å	1.485	1.458	1.466	1.390	1.390	1.401	+0.076
e/Å	1.362	1.349	1.346	1.454	1.411	1.415	−0.074
f/Å	1.478	1.458	1.460	1.389	1.388	1.381	+0.079
g/Å	1.415	1.402	1.397	1.458	1.438	1.438	−0.040
h/Å	1.404	1.385	1.391	1.377	1.367	1.355	+0.027
i/Å	1.417	1.414	1.401	1.453	1.445	1.446	−0.037
j/Å	1.434	1.435	1.457	1.371	1.350	1.345	+0.087

[a] The bond lengths for the rings each correspond to the mean of the two related dimensions.

dye. Theoretical modelling has confirmed that the counterion must be appropriately placed to stabilise either the aromatic or quinonoid form. It has important implications for both molecular scale electronics and nonlinear optics showing, for the first time, that the molecular dipole is independent of the molecular orientation.

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