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HETEROCYCLES AS DONOR AND ACCEPTOR UNITS IN PUSH–PULL CONJUGATED MOLECULES. PART 1

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The synthesis and spectroscopic investigation of a number of push–pull ethenes in which the donor moiety is represented by a π-excessive five-membered heterocycle (pyrrole, indole and thiophene) and the acceptor group is a π-deficient heterocyclic azine ring (pyridine, pyrazine, pyrimidine, pyridazine) are described. The intramolecular charge transfer in both the neutral compounds and the corresponding *N*-alkylpyridinium triflates is discussed and confirmed on the basis of three different descriptors, $\Delta\lambda_{Ph}^{Het}$, $\Delta\lambda_{n}^{+}$, and $\Delta\lambda_{solv2}^{solv1}$, that take into account the substitution of a phenyl with a heterocyclic donor ring, charge effects and solvatochromism, respectively. According to the $\Delta\lambda_{Ph}^{Het}$ descriptor, the intramolecular charge transfer in the described diheteroarylethenes increases upon increasing the electron-withdrawing capacity of the acceptor, sustained by the presence of either more than one nitrogen atom or the positive charge in the heterocyclic azine. The described pyridinium derivatives belong to the rarely investigated class of dimethine cyanine dyes. The response of the ^{13}C and ^{15}N NMR chemical shift data appears to be less clear because of the low sensitivity of the NMR probes to remote substitution. © 1997 John Wiley & Sons, Ltd.

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INTRODUCTION

Push–pull molecules[1,2] (**1**) are the subject of renewed interest because, being dipolar, they may present relevant hyperpolarizabilities, a property which is a prerequisite for molecules that are candidate components of non-linear optical (NLO) materials.[3] In the absence of steric effects, the extent of the contribution of the dipolar resonance structure **1′** depends on the donating strength of the donor group D and the electron-withdrawing power of the acceptor group A. Very often the A and D groups are primary organic functionalities: amino, dialkylamino, ether and oxide (O^-) groups act as donors and nitro, carbonyl and cyano groups as acceptors. These substituents are present in *p*-disubstituted benzenes, such as *p*-nitro-*N*,*N*-dimethylaniline and congeners,[4] and in push–pull ethenes such as 4-dimethylamino-4′-nitrostilbene (DANS, **2**).[5] Positively charged heterocycles, mainly azinium and azolium ions, have been used as acceptors in hemicyanines and merocyanines.[6] However, they have been used as donors much less frequently, although benzodithiole has been incorporated in polyenals[7] that have been proposed for second-harmonic generation (SHG).

1 **1'**

No examples have yet been reported of systematic studies aimed at evaluating whether push–pull properties can be realized when a π-deficient and a π-excessive heterocycle are the acceptor group A and the donor group D, respectively: only recently the issue has been addressed in the perspective on NLO materials.[8] On the basis of these premises, we investigated whether ethenes bearing at the α-position an azine ring as an acceptor and the β-position an *N*-methylpyrrol-2-yl ring as a donor could have high conjugative π-delocalization and push–pull properties. For example, compound **4** could be considered a heterocyclic analogue of **2** if the dipolar resonance structure **4′** can contribute substantially to the description of the bonding of the system.

With reference to acceptors, we have shown previously[9–11] that heterocyclic azines (pyridine, pyrazine, pyridazine and pyrimidine) are strong acceptor groups in α-azinylmethylcarbanions. Ranking their electron-withdrawing power on the same scale of primary π-deficient organic functionalities, the 4-pyrimidyl group is the most powerful accepting ring amongst the azines and has a charge demand[11]

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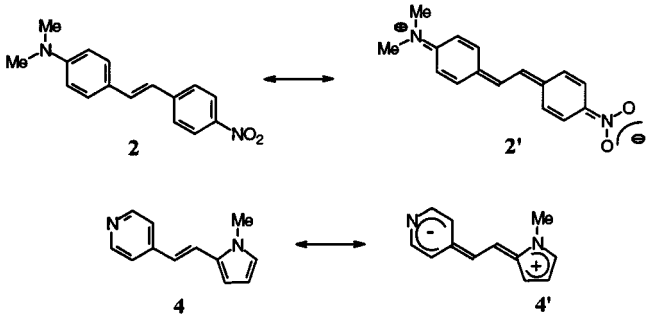


2 **2'**

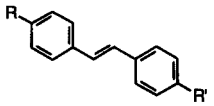
4 **4'**

$c_X = 0{\cdot}501$, equivalent to that of the acetyl functionality ($c_X = 0{\cdot}509$).[12] Alternatively, the σ_{R^-} value of the 4-pyrimidyl group, extrapolated according to a previously reported relationship,[12] is *ca* 0·48, very close to the figure obtained for the *p*-nitrophenyl ring (0·52).[13]

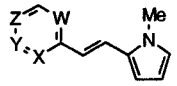
Much less is known about heterocyclic donors since quantitative ranking is available neither on the same scale as above for π-deficient systems nor on a similar one having carbenium ions instead of carbanions as a reference. Given their π-excessive[14] nature, five membered monoheterocycles (furan, thiophene and pyrrole) are π-donor substituents as established by their σ_R values[15] and oxidation potentials,[16] and there is no doubt that pyrrole is the most π-excessive system of the three.

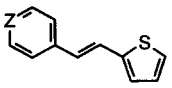
We report here the synthesis and results obtained with diheteroarylethenes **4**–**9**.

Compounds **4** and **5** were considered particularly interesting because, by alkylating the pyridyl nitrogen atom, we could realize an easy entry into the class of unsymmetrical cyanine dyes that, together with merocyanines and hemicyanines, exhibit considerable interest for NLO properties.[6] The positive charge in the alkyl triflates **10**–**12**, besides increasing the electron-withdrawal of the pyridyl ring and thus favoring the push–pull characteristics of the systems,



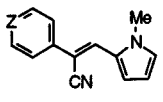
2 : R = Me_2N R' = NO_2
3 : R = Me_2NH^+ R' = NO_2

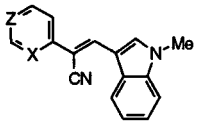




4 : Z = N — Y = X = W = CH
5 : X = N — Z = Y = W = CH
6 : Y = W = N — X = Z = CH
7 : X = Y = N — W = Z = CH
8 : X = Z = N — Y = W = CH
10 : Z = MeN^+ $CF_3SO_3^-$ — X = Y = W = CH
11 : Z = $C_{16}H_{33}N^+$ $CF_3SO_3^-$ — X = Y = W = CH
12 : X = MeN^+ $CF_3SO_3^-$ — Z = Y = W = CH

9 : Z = N
13 : Z = MeN^+ $CF_3SO_3^-$





14 : Z = N
17 : Z = MeN^+ $CF_3SO_3^-$

15 : Z = N X = CH
16 : Z = CH X = N
18 : Z = MeN^+ $CF_3SO_3^-$ X = CH

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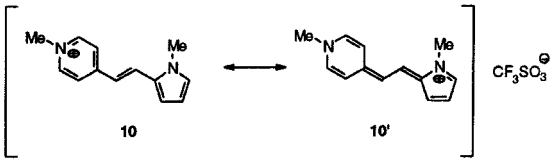


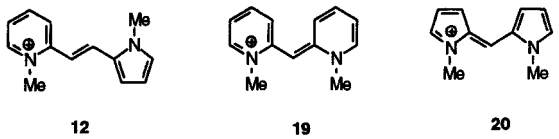
can in principle partition between the two different *N*-Me groups of the two heterocycles.

Compounds **10**–**12** are referred to as *unsymmetrical* cyanines but, according to the most common nomenclature,[17–19] it is convenient to consider them as dimethine cyanines, a rarely investigated class of dyes.[17–19] It has been shown many years ago[20] that in this class of compounds the longest wavelength absorptions are ipsochromically shifted in comparison with the average of absorptions of the two symmetrical cyanines having the same terminal heterocycles present in the unsymmetrical cyanine. We expect, therefore, that the λ_{MAX} of **12** will be blue shifted in comparison with its symmetric structural isomer **19** and of pyrrolocyanine **20**. The above electronic property is highly recommended for NLO materials because provides wider transparency.[21] For completeness, we also investigated the triflate **13** associated with the thienyl derivative **9**.

To enhance the electron withdrawal at the α-terminus of the ethene fragment, we further examined the α-cyanosubstituted systems **14**–**16** and their corresponding triflates **17** and **18**.

In order to obtain evidence for the contribution of the primed dipolar structures, we followed two approaches. First, we planned a UV–visible spectroscopic investigation based on three different descriptors, $\Delta\lambda_{Ph}^{Het}$, $\Delta\lambda_{n}^{+}$ and $\Delta\lambda_{solv2}^{solv1}$, which take into account the substitution of a phenyl with a heterocyclic donor ring, charge effects and solvatochromism, respectively; particular attention was paid to the solvatochromism of all of the prepared compounds, since push–pull molecules are expected to present this phenomenon.[22] Second, despite the known low sensitivity of ^{13}C and ^{15}N chemical shifts to remote structural variation,[23] we tried to exploit their reported dependence on local π-electron density on carbon[24] and nitrogen[25] by recording the ^{13}C and ^{15}N NMR spectra of some products and comparing them with those of some selected models in which charge transfer is inconceivable.

With reference to the $\Delta\lambda$ descriptors, our overall results provide evidence that there is a strong charge-transfer interaction between the donor and the acceptor heterocycle. In particular, the solvatochromism in some neutral compounds is of the same order of magnitude as that presented by DANS, a molecule that, together with *p*-nitroaniline, is often referred to as a standard for non-linear optical properties.[5] During the course of the present study, Pan *et al.*[8] reported that compound **9** has a β_μ value of 33×10^{-30} esu, to be compared with a value of 28×10^{-30} esu for *p*-nitroaniline. This result, together with the high efficiency for two-photon pumped frequency-upconversion lasing presented by the dimethine cyanine **10**,[26] bears witness to the extraordinary interest that the class of molecules we describe here may have as precursors of materials for NLO applications. Considerably larger solvatochromism is found in the corresponding unsymmetrical dimethine cyanines. Although the electronic absorption characteristics and solvatochromic responses of the described diheteroarylethenes and dimethine cyanines leave little doubt about the contribution of intramolecular charge-transfer dipolar structures, the NMR probes were found to be much less sensitive than UV–Vis spectroscopy, and therefore provided less clear responses with some of them offering only circumstantial evidence of the resonance dipolar primed structures.



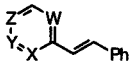
RESULTS

Compound synthesis

Compounds **4**–**8** were prepared in DMF from the corresponding methyl azine and *N*-methylpyrrole-2-carboxyaldehyde in the presence of sodium hydride. Similarly, compounds **14**–**16** were prepared in *t*-BuOH starting from the corresponding pyridylacetonitrile and either *N*-methylpyrrole-2-carboxyaldehyde or *N*-methylindolyl-3-carboxyaldehyde in the presence of potassium *tert*-butoxide. Compound **9** was obtained by Wittig–Horner coupling of pyridyl-4-carboxyaldehyde and diethyl 2-thenylphosphonate. The pyridinium triflates **10**–**13**, **17** and **18** were prepared by reacting the relevant azinylethylenes with the appropriate alkyl triflate in benzene or acetone.

Spectroscopic and solvatochromic data

To evaluate the effect of pyrrole as a donor heterocycle, we took 4-styrylpyridine (**21**) as a model for compound **4** and 2-styrylpyridine (**22**) as a model for compound **5**; corre-



21 : Z = N X = Y = W = CH
22 : X = N Z = Y = W = CH
23 : Z = MeN^+ X = Y = W = CH
24 : X = MeN^+ Z = Y = W = CH
25 : Y = W = N X = Z = CH
26 : X = Y = N W = Z = CH
27 : X = Z = N Y = W = CH

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spondingly, the methyl derivatives **23** and **24** are models for the methylated pyrrolyl derivatives **10** and **12**. On the same grounds, the styryl derivatives **25**–**27** are considered the phenyl analogs of compounds **6**–**8**. Table 1 lists the longest wavelength absorption maxima, λ_{max}, for all of the prepared compounds, together with those of the model compounds **21**–**27** and DANS, both as the neutral species **2** and in its protonated form **3**. Spectra were recorded in both MeOH and $CHCl_3$, and indication of the solvatochromic effect is provided by the $\Delta\lambda^{solv1}_{solv2} = (\lambda_{max})_{solv1} - (\lambda_{max})_{solv2}$.

Other relevant $\Delta\lambda$ values are collected in Tables 2 and 3. The values $\Delta\lambda^{+}_{n} = (\lambda_{max})_{cation} - (\lambda_{max})_{neutral}$ in Table 2 provide an indication of the effects obtained by substituting the alkylpyridinum (or alkylammonium) ion for the corresponding base, and the values $\Delta\lambda^{Het}_{Ph} = (\lambda_{max})_{Het} - (\lambda_{max})_{Ph}$ in Table 3 measure the effect of substituting the heterocyclic (pyrrolyl and thienyl) for the phenyl ring in the model compounds **21**–**27**.

The data in Table 1 indicate that the neutral compounds **4**–**9** and **14**–**16** generally have weak solvatochromism, although compounds **4**, **14** and **15** have a $\Delta\lambda^{solv1}_{solv2}$ value that is of the same order of magnitude as that of DANS (**2**). However, cations **10**–**12** have an appreciable solvatochromism, with their $\Delta\lambda^{solv1}_{solv2}$ being in the range 14–22 nm. The same $\Delta\lambda$ value drops to a few nm for cations **13**, **17** and **18**.

Table 2 shows that the $\Delta\lambda^{+}_{n}$ values fall into two ranges, following the size of the shift. The *N*-methylpyridinium compounds **23** and **24** are bathochromically shifted in comparison with their neutral counterparts **21** and **22** by *ca* 25–35 nm; a slightly larger, but comparable, shift is also found on going from **9** to **13**. Unlike **13**, cations **10**, **12**, **17** and **18** show a larger shift in comparison with the corresponding neutrals, ranging from a minimum of 61 nm (for **14→17**) to a maximum of 82 nm (for **4→10**). This last value approaches the shift observed on going from DANS hydrochloride to its neutral (95 nm). The effect of charge measured in $CHCl_3$ on the cetyl derivative **11**, which is soluble in this solvent, is even larger (103 nm).

The data given in Table 3 show the effect of substituting

Table 1. Long-wavelength UV–Visible absorption maxima of compounds **2**–**27** in different solvents

	λ_{max} (nm)				
Compound	MeOH (log ε)	$CHCl_3$	H_2O	$\Delta\lambda^{solv1}_{solv2}$ [a]	Notes
2	430[b]	435·5[c]		−5·5	d
3	335[b]				d
4	362 (4·34)	356		+6	e
5	355 (4·30)	356		−1	e
6	381 (4·23)	381·5		−0·5	e
7	360 (4·35)	360		0·0	e
8	380 (4·41)	377		+3	e
9	330 (4·43)	332		−2	e
10	444 (4·50)		422	−22	e
11	445 (4·55)	459		−14	e
12	423 (4·15)		406	−17	e
13	377 (4·16)		371	−6	e
14	389 (4·68)	394		−5	e
15	399 (4·46)	392		+7	e
16	390 (4·50)	392		−2	e
17	450 (4·70)		442	−8	e
18	463 (4·50)		455	−8	e
21	307	300		+7	b, f
22	310	314		−4	b, f
23	342		335	−7	g
24	338		334	−4	g
25	320				h
26	290				h
27	311				h

[a] $\Delta\lambda = \lambda_{max}$ (polar solvent) − λ_{max} (non-polar solvent): positive $\Delta\lambda$ values mean positive solvatochromism.
[b] Ref. 27.
[c] Ref. 28.
[d] In EtOH instead of MeOH.
[e] This work.
[f] Ref. 29.
[g] Ref. 30.
[h] Ref. 31.

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Table 2. Charge-promoted displacements $\Delta\lambda_n^+$ of the longest wavelength UV–visible absorption maximum

Entry	Compounds	$\Delta\lambda_n^{+\,a,\,b}$
1	**2→3**	−95[c]
2	**4→10**	+82
3	**4→11**	+83
4		+103[d]
5	**5→12**	+68
6	**9→13**	+47
7	**14→17**	+61
8	**15→18**	+64
9	**21→23**	+35
10	**22→24**	+28

[a] $\Delta\lambda_n^+ = (\lambda_{max})_{cation} - (\lambda_{max})_{neutral}$ (nm).
[b] In MeOH if not specified otherwise.
[c] In EtOH.
[d] In $CHCl_3$.

Table 3. Bathochromic shift (nm) of long-wavelength UV–visible absorption bands in MeOH obtained by substituting heterocyclic for phenyl rings

Entry	Comnpounds	$\Delta\lambda_{Ph}^{Het\,a}$
1	**21→4**	+55
2	**22→5**	+45
3	**25→6**	+61
4	**26→7**	+70
5	**27→8**	+69
6	**21→9**	+23
7	**23→10**	+102
8	**24→12**	+85
9	**23→13**	+35

[a] $\Delta\lambda_{Ph}^{Het} = (\lambda_{max})_{Het} - (\lambda_{max})_{Ph}$

a heterocycle for a phenyl ring. Substitution of the thienyl for the phenyl ring in compound **21** to give **9** causes a weak displacement ($\Delta\lambda_{Ph}^{Th} \approx 24$ nm) that is almost doubled in the corresponding cation **13**. Substitution of the pyrrolyl for the phenyl ring causes a much stronger bathochromic displacement for compounds **4** and **5** ($\Delta\lambda_{Ph}^{Pyrr} \approx 50$ nm), a value that is doubled in the corresponding cation **10**. The observed bathochromic shift $\Delta\lambda_{Ph}^{Het}$ increases on going from pyridyl derivatives **4** and **5** to diazinyl compounds **7**–**9**.

Table 4 shows the ^{13}C and ^{15}N NMR shifts of the push–pull ethenes **4**–**8** and dimethine cyanines **10** and **11**; in addition, the available literature data are given for ^{13}C and ^{15}N NMR chemical shift values of azine rings of styrylazines **21**–**23** and **25**–**27**. ^{13}C NMR shift assignments for azine carbon atoms have been based on known shift patterns:[32] in accord with the results reported for styrylazines,[33] carbons C-α and C-β have been identified assigning the lowfield value to the β-carbon. The arbitrary numbering reported in the general formulae **A** and **B** in Table 4 has been adopted to make comparison easier between the analogous positions of the various rings.

DISCUSSION

Intramolecular charge transfer in neutral and charged ethenes

Electronic and solvatochromic probes

To obtain evidence for the resonance contribution of the primed dipolar structures, we evaluated the composite response of the three descriptors $\Delta\lambda_{Ph}^{Het}$, $\Delta\lambda_n^+$ and $\Delta\lambda_{solv2}^{solv1}$. There is no doubt that the $\Delta\lambda_{Ph}^{Het}$ descriptor provides strong evidence for the donor interaction of pyrrole and thiophene with the pyridyl ring: substitution of the phenyl in styrylpyridines **21** and **22** by the *N*-methylpyrrol-2-yl in **4** and **5** or the thien-2-yl ring in **9** causes a substantial bathochromic shift, ranging from 23 to 55 nm, that indicates the sizeable electronic interaction of the two heterocycles mediated by the intervening double bond. The pyrrolyl derivatives show a larger shift than the thienyl compound and provide evidence that in the former case the intramolecular charge transfer is easier because pyrrole has a stronger donor property than thiophene. The contribution of the pyrrolyl ring to bathochromic displacement is not constant, but increases if the pyridyl is substituted by the diazinyl rings. This result is in accord with the increased charge demand of diazines in comparison with pyridine. Comparison of the neutral pyrrole and thiophene donor-substituted systems **4**, **5** and **9** with the styrylpyridines **21** and **22** can be extended to the corresponding cations **10**, **12** and **13** with the styryl-*N*-methylpyridinium salts **23** and **24**. In relation to the neutral compounds, the bathochromic effect exerted by the pyrrole and thiophene rings in the pyridinium derivatives **10**, **12** and **13** increases noticeably (entries 7–9 in Table 3), once it is taken into account that the presence of the positive charge shifts the absorption of **23** and **24** by 35 and 28 nm, respectively, in relation to the free bases **21** and **22**. This once again suggests that the intramolecular charge transfer between the pyrrole and the pyridyl ring increases with the increasing electron-withdrawing capacity of the acceptor, sustained in this case by the presence of a positive charge.

The $\Delta\lambda_n^+$ variation for compound **4** on going to either **10** or **11** is of the same order of magnitude as that found on going from **3** to **2**. The protonation of DANS prevents any intramolecular charge transfer, but the alkylation of **4** stimulates the charge transfer as much as it is depressed in protonated DANS. The long-wavelength absorption of compound **12** ($\lambda_{max} = 423$) does not reach the values for symmetrical cyanine dyes[17–19] (e.g. for **19**[34] $\lambda_{max} = 461$, 478), but in view of the high $\Delta\lambda_n^+$ values found for this and the similar compounds **10** and **11**, it seems appropriate to state that extensive delocalization exists in these dimethine cyanines.

Compounds **14**–**16** were synthesized on the basis of the hypothesis that the cyano group would greatly help intramolecular charge transfer interaction. In relation to **4**, compound **14** does show a bathochromic shift of about 30 nm, but altogether does not seem to be much more

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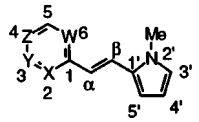
efficient than a second nitrogen atom in the azine nucleus as in the pyrimidyl derivative **8**. Finally, when comparing the pyrrole and the indole rings (Table 1), the latter does not appear to be a better electron donor than the pyrrole residue.

Although compounds **4** and **5** have similar $\Delta\lambda_{Ph}^{Het}$ values (55 and 45 nm), their solvatochromic responses are different: compound **4** and DANS have a similar solvatochromic effect, whereas compound **5** has practically no solvatochromism. Conversely, the solvatochromism of the corresponding *N*-methylpyridinium compounds **10**–**12** is 3–4 times as large as that of DANS. The data for $\Delta\lambda_{Ph}^{Het}$ and $\Delta\lambda_{solv2}^{solv1}$ do not therefore vary monotonically. The data in Table 1 further indicate that the presence of the *aza* group *para* to the ethylenic fragment favours solvatochromism more than in the *ortho* position. This observation is valid not only when considering the 2-pyridyl vs the 4-pyridyl substitution as in compounds **4** and **5**, but also when considering that an *ortho* aza group is always present in all the other azine derivatives **6**–**8**. The variation of the dipole moment in the ground and excited states of molecules is the important phenomenon involved in solvatochromism; this event has little to do with delocalization, and thus with $\Delta\lambda_{Ph}^{Het}$. This means that the different response of $\Delta\lambda_{Ph}^{Het}$ and $\Delta\lambda_{solv2}^{solv1}$ may be explained on the basis of the different dependence of the two descriptors on structural connectivity.

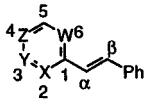
^{13}C and ^{15}N NMR probes

It is worth examining the ^{13}C and ^{15}N NMR data separately, and the ^{13}C data in Table 4 can also be treated using two different approaches. First, the ^{13}C shifts of the azine moiety of the diheteroarylethenes **4**–**8** can be compared with those of the styrylazines **21**, **22** and **25**–**27**. It can be seen that the substitution of the π-donating pyrrol-2-yl for the phenyl ring does not induce any variation in the ^{13}C azine shifts, which are almost identical in the two series. In contrast, the C-α and C-β shifts of the ethene bridge evidently respond to the π-donation of the pyrrolyl ring, as both shifts move to high field by 3–7 and 4–12 ppm in compounds **4**–**8**. Second, but more significantly, the most meaningful comparison is that of neutral compound **4** with the corresponding *N*-methylpyridinium derivatives **10** and **11**.

Table 4. ^{13}C NMR shifts (ppm)[a] (roman type) and ^{15}N NMR shifts (ppm)[b] (italic type) of compounds **4**–**8**, **10**, **11**,[c, d] **21**–**23** and **25**–**27**



A(4 - 8, 10, 11)



B(21-23, 25-27)

		Azine ring positions								Pyrrole ring positions				
Compound	Solvent	1	2	3	4	5	6	α	β	1′	2′	3′	4′	5′
4	$CDCl_3$	145·1	120·1	149·9	*299·8*	149·9	120·1	121.1	122·2	130·8	*143·2*	124·9	108·6	108·7
4	DMSO	145·3	120·4	147·8	*309·8*	147·8	120·4	121·3	122·2	130·7	*150·6*	125·4	108·5	108·5
5	$CDCl_3$	155·9	*294·6*	149·5	121·9[e]	136·4	121·2	120·7	124·3	131·4	*143·6*	124·5	108·0	108·5
6	$CDCl_3$	151·7	144·0	*310·0*	141·7	144·0	*325·6*	119·7	122·9	131·0	*144·1*	125·2	108·1	108·8
7	$CDCl_3$	158·3	*382·6*	*391·6*	148·8	126·2	123·0	120·4	124·0	130·8	*144·3*	125·3	108·8	109·2
8	$CDCl_3$	162·5	*278·3*	158·6	*272·8*	157·0	118·4	120·7	126·1	130·5	*145·0*	125·1	109·2	110·3
10	DMSO	153·3	122·1	144·3	*188·0*	144·3	122·1	117·4	129·5	130·4	*154·3*	128·7	112·3	109·9
11	$CDCl_3$	154·5	122·9	142·6	*202·0*	142·6	122·9	116·5	130·4[f]	130·5	*143·0*	129·3	113·8	110·8
11	DMSO	153·6	122·4	143·4	*199·0*	143·4	122·4	117·4	129·7	130·5	*153·0*	128·8	112·4	110·0
21[g]	$CDCl_3$	144·1	120·5	149·8	*312·9*[h]	149·8	120·5	125·6	132·7					
22[g]	$CDCl_3$	155·1		149·2	121·6	136·0	121·7	127·6	132·3					
23	DMSO				*194·05*[h]									
25[g]	$CDCl_3$	151·0	143·3		142·4	143·9		123·7	134·7					
26[g]	$CDCl_3$	157·8			149·2	126·1	123·6	124·7	134·7					
27[g]	$CDCl_3$	161·8		158·5		157·0	118·3	123·7	134·7					

[a] Relative to Me_4Si (0·0 ppm).
[b] Relative to liquid NH_3 (0·0 ppm), 380·23 ppm from neat nitromethane.
[c] 0·2 M solutions.
[d] Positions are identified according to the arbitrary numbering given in formulae **A** and **B**.
[e, f] Assignments may be interchanged.
[g] From Ref. 28.
[h] In DMSO, from Ref. 23.

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The low-field shift suffered by carbons C-3′ and C-4′ of the pyrrole ring and the corresponding high-field shift of the C-3 and C-5 of the pyridyl ring are evidence for greater push–pull interaction in **10** and **11** than in **4**, with electrons flowing from the five- to the six-membered ring. The displacements are not dramatic but are in the right direction. As a partial conclusion, we can say that, in the neutral systems, π-donation of the pyrrolyl ring is experienced by the relatively close ^{13}C carbons of the bridge, but not by the relatively remote carbons of the azine moieties. These carbon atoms, as well as those of the pyrrolyl ring, become sensitive when a positive charge is placed on the acceptor ring.

Evaluation of the ^{15}N chemical shift displacements appears to be more complex, and so it is worth discussing the responses of the pyridyl and pyrrolyl nitrogen atoms separately. In compounds **4** and **5**, the ^{15}N shift in $CDCl_3$ of the pyridyl moiety is about 10 ppm to high field of the shift of unsubstituted pyridine ($\delta^{15}N = 310$ ppm vs NH_3).[35] An analogous displacement is found in DMSO, although the shift of unsubstituted pyridine in this solvent is displaced towards low field ($\delta^{15}N = 317$ ppm).[35] In comparison with styrylpyridine (**21**), the shift in **4** is 13 ppm to high field. In comparison with styrylpyridinium iodide (**23**), the pyrrolylpyridium salt **10** shows a high-field displacement of 6 ppm. These changes are relatively small, but can be safely interpreted[24] as evidence for a higher π-electron density on the pyridyl nitrogen of **4** and **5** than on the unsubstituted pyridine and styrylpyridine, and on the pyrrolylpyridinium cation **10** than on the styrylpyridinium iodide **23**. Although carbon shifts do not vary on going from styrylpyridine to pyrrolylethenylpyridine, nitrogen shifts do, although their sensitivity to remote structural variation remains low, as Srinivasan *et al*.[23] found in relation to phenyl-substituted styrylpyridines. The case of the ^{15}N NMR data of the pyrrolyl group in **4**, **5** and **10** is different. In $CDCl_3$, the ^{15}N shift of the pyrrole moiety in **4** and **5** is about 6 ppm to high field of the shift recorded for *N*-methylpyrrole in the same solvent ($\delta^{15}N = 149{\cdot}33$ ppm)[35] but, in DMSO, the shifts of **4** and *N*-methylpyrrole ($\delta^{15}N = 150{\cdot}13$ ppm)[35] almost coincide. Thus, although the ^{15}N shifts of **4** are solvent dependent, the ^{15}N shift of *N*-methylpyrrole is not. Furthermore, pyrrole ^{15}N shifts do not vary on going from the neutral **4** to the pyridinium cations **10** and **11**. It appears difficult to account for these pyrrolyl ^{15}N NMR data since no ^{15}N shift–π-electron density relationships are available for pyrrole-type nitrogen atoms, unlike the case of the reliable and successful relationships involving the pyridyl-type nitrogen atom in various heterocycles.[25c, 36]

CONCLUSION

We have shown that π-excessive and π-deficient heterocycles can successfully act as donors and acceptors, respectively in push–pull systems, and may conveniently substitute primary organic functionalities. The three descriptors $\Delta\lambda_{Ph}^{Het}$, $\Delta\lambda_n^+$ and $\Delta\lambda_{solv2}^{solv1}$ provide unequivocal evidence of intramolecular charge transfer from the five-to the six-membered azine rings; this transfer is considerably more important for pyrrole than for thiophene derivatives, and is amplified by increasing the electron withdrawal of the acceptor, as in diazine substituted ethenes. Both the $\Delta\lambda_{Ph}^{Het}$ descriptor and NMR data indicate that the intramolecular charge transfer is amplified in the pyridinium ions and this conclusion is also strongly supported by the $\Delta\lambda_n^+$ data. Although offering a good qualitative tool for interpreting our results and validating our initial hypothesis about push–pull properties, the three descriptors do not provide a quantitative energy-based rank associated with the intramolecular charge transfer. Any quantitative comparison between DANS or any other known push–pull representative molecule and any of the compounds that we have described here must await a different and more sophisticated approach.[37]

EXPERIMENTAL

^1H NMR specta were recorded on Varian XL-300 and Bruker 300 AC instruments, using Me_4Si as internal standard. ^{13}C NMR spectra were recorded at 27 °C on a Varian XL-300 spectrometer, operating at 75·45 MHz and using 0·2 M solutions in DMSO. ^{15}N NMR spectra were recorded at 27 °C on a Bruker AMX 500 WB spectrometer, operating at 50·66 MHz and using 0·2 M solutions in DMSO. ^{13}C NMR shifts were measured relative to Me_4Si and ^{15}N NMR shifts were measured relative to liquid NH_3 (0·0 ppm), 380·23 ppm from neat nitromethane. For ^{15}N measurements, two experiments were adopted. INEPT spectra were obtained with the following acquisition parameters: spectral width 26 316 Hz, 64K data points, pulse delay 4 s, pulse angle 90° for 17 μs, zero filling (once), line broadenings of 10 Hz and number of transients of 30 000. HMQC spectra were recorded using the pulse sequence INVBTP (Bruker software). In general, 256 × 1K data sets were zero filled to 1K × 1K using 600 scans per increment and spectral widths of 6000 and 26 006 Hz were employed in the ^1H and ^{15}N domains, respectively. [$^2H_6$]Me_2SO solvent provided the internal deuterium lock. Coupling constant values, *J*, are given in Hz throughout UV–visible spectra were recorded on a Perkin-Elmer Lambda 6 UV/VIS spectrometer. Elemental analyses were performed on a Perkin-Elmer Model 240 instrument by the microanalysis laboratory of our department. Melting points are uncorrected. Acetone was dried over Na_2SO_4 (4 h). Sublimations were performed at 50–70 °C under vacuum (0·01–0·02 mmHg).

Materials. Anhydrous THF was obtained by continuous distillation over sodium sand, in the presence of benzophenone and under nitrogen until the blue of sodium ketyl was permanent. Drying of the solvents was performed over Na_2SO_4. *N*-methylpyrrole-2-carboxyaldehyde (Fluka), thiophene-2-carboxyaldehyde (Fluka) and methylazines (Fluka and Aldrich) were commercial products. Diethyl 2-thienyl-

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methylphosphonate was prepared according to known procedures.[38]

*1-(Pyridin-4-yl)-2-(*N-*methylpyrrol-2-yl)ethene (4).* A solution of 4-picoline (0·860 g, 9·16 mmol) in anhydrous DMF (4 ml) was added under nitrogen to a suspension of sodium hydride (60% dispersion in mineral oil, 9·16 mmol) in the same solvent (10 ml). After stirring for 2 h at 60 °C, a solution of *N*-methylpyrrole-2-carboxyaldehyde (1·00 g, 9·16 mmol) in anhydrous DMF (6 ml) was then added to the red solution of the anion. After stirring for 7 h at the same temperature, the reaction mixture was poured on to ice (60 ml) to give a yellow solid which was collected and identified as the practically pure compound (0·930 g, 5·05 mmol, 55·1%), m.p. 126–127 °C (EtOH–H_2O) (found: C, 78·4; H, 6·6; N, 15·45. Calc. for $C_{12}H_{12}N_2$: C, 78·2; H, 6·6; N, 15·2%), δ_H ($CDCl_3$) 8·50 (2 H, d, $J_{2,3}$ 5·9, 2-H and 6-H), 7·26 (2 H, d, 3-H and 5-H), 7·15 (1 H, d, $J_{\alpha\beta}$ 16·1, α-H), 6·74 (1 H, d, β-H), 6·67 (1 H, dd, $J_{4',5'}$ 2·0, 5′-H), 6·57 (1H, dd, $J_{3',5'}$ 1·7, 3′-H), 6·16 (1 H, dd, $J_{4',3'}$ 2·7, 4′-H), 3·70 (3 H, s, N-Me).

*1-(Pyridin-2-yl)-2-(*N-*methylpyrrol-2-yl)ethene (5).* A solution of 2-picoline (1·71 g, 18·3 mmol) in anhydrous DMF (10 ml) was added under nitrogen to a suspension of sodium hydride (60% dispersion in mineral oil, 18·3 mmol) in the same solvent (18 ml). After stirring for 2 h at 60 °C, a solution of *N*-methylpyrrole-2-carboxyaldehyde (2·00 g, 18·3 mmol) in anhydrous DMF (12 ml) was then added to the red solution of the anion. After stirring for 5 h at the same temperature, the reaction mixture was poured on to ice (100 ml) to give a yellow solid which was collected and identified as the practically pure compound (0·920 g, 4·99 mmol, 27·2%), m.p. 93–94 °C (EtOH) (found: C, 78·5; H, 6·4; N, 15·1. Calc. for $C_{12}H_{12}N_2$: C, 78·2; H, 6·6; N, 15·6%); δ_H ($CDCl_3$) 8·53 (1 H, dd, $J_{5,6}$ 4·9, 6-H), 7·59 (1 H, dd, $J_{4,6}$ 1·8, 4-H), 7·56 (1 H, d, J, 15·8, α-H), 7·22 (1 H, d, $J_{3,4}$ 8·2, 3-H), 7·06 (1 H, dd, $J_{4,5}$ 7·5, 5-H), 6·87 (1 H, d, β-H), 6·66 (1 H, dd, $J_{4',5'}$ 2·3, 5′-H), 6·58 (1 H, dd, $J_{3',5'}$ 1·5, 3′-H), 6·15 (1 H, dd, $J_{3',4'}$ 3·4, 4′-H), 3·67 (3 H, s, N-Me).

*1-(Pyrazinyl)-2-(*N-*methylpyrrol-2-yl)ethene (6).* A solution of methylpyrazine (0·860 g, 9·16 mmol) in anhydrous DMF (4 ml) was added under nitrogen to a suspension of sodium hydride (60% dispersion in mineral oil, 9·20 mmol) in the same solvent (10 ml). After stirring for 1 h at 60 °C, a solution of *N*-methylpyrrole-2-carboxyaldehyde (1·00 g, 9·16 mmol) in anhydrous DMF (6 ml) was then added to the red solution of the anion. After stirring for 5 h at 50 °C, the reaction mixture was poured on to ice (50 ml) to give a yellow solid which was collected, washed with water, and identified as the practically pure compound (0·670 g, 3·61 mmol, 39·5%), m.p. 75–77 °C (after sublimation) (found: C, 71·5; H, 6·2; N, 22·6. Calc. for $C_{11}H_{11}N_3$: C, 71·3; H, 6·0; N, 22·7%); δ_H ($CDCl_3$) 8·48 (1 H, d, $J_{5,6}$ 1·5, 6-H), 8·45 (1 H, dd, 5-H), 8·29 (1 H, d, $J_{3,5}$ 2·4, 3-H), 7·67 (1 H, d, $J_{\alpha,\beta}$ 16·1, α-H), 6·85 (1 H, d, β-H), 6·69 (1 H, dd, $J_{4',5'}$ 1·9, 5′H), 6·64 (1 H, dd, $J_{3',5'}$ 1·5, 3′-H), 6·17 (1 H, dd, $J_{3',4'}$ 3·4, 4′-H), 3·73 (3 H, s, N-Me).

*1-(Pyridazin-3-yl)-2-(*N-*methylpyrrol-2-yl)ethene (7).* A solution of 3-methylpyridazine (0·860 g, 9·16 mmol) in anhydrous DMF (4 ml) was added under nitrogen to a suspension of sodium hydride (60% dispersion in mineral oil, 9·20 mmol) in the same solvent (10 ml). After stirring for 30 min at 60 °C, a solution of *N*-methylpyrrole-2-carboxyaldehyde (1·00 g, 9·16 mmol) in anhydrous DMF (6 ml) was then added to the solution of the anion. After stirring for 3 h at 50 °C, the reaction mixture was poured on to ice (70 ml) and extracted with CH_2Cl_2 (3 × 30 ml). The extracts were washed with water and the solvent was removed from the dried extracts to leave a dark solid (1·21 g). The product was purified by chromatography on silica gel (AcOEt–CH_2Cl_2, 1:1) to give a yellow solid (0·720 g, 3·89 mmol, 42·4%), m.p. 98–100 °C (after sublimation) (found: C, 71·4; H, 6·3; N, 23·0. Calc. for $C_{11}H_{11}N_3$: C, 71·3; H, 6·0; N, 22·7%); δ_H ($CDCl_3$) 8·96 (1 H, d, $J_{5,6}$ 4·7, 6-H), 7·77 (1 H, d, $J_{\alpha,\beta}$ 15·9, α-H), 7·34–7·44 (2 H, m, 4-H and 5-H), 6·94 (1 H, d, β-H), 6·70 (1 H, dd, $J_{4',5'}$ 3·2, 5′-H), 6·65 (1 H, d, $J_{3',4'}$ 3·9, 3′-H), 6·18 (1 H, dd, 4′-H), 3·73 (3 H, s, N-Me).

*1-(Pyrimidin-4-yl)-2-(*N-*methylpyrrol-2-yl)ethene (8).* A solution of 4-methylpyrimidine (1·00 g, 10·6 mmol) in anhydrous DMF (6 ml) was added under nitrogen to a suspension of sodium hydride (60% dispersion in mineral oil, 9·20 mmol) in the same solvent (10 ml). After stirring for 1 h at 40 °C, a solution of *N*-methylpyrrole-2-carboxyaldehyde (1·00 g, 9·16 mmol) in anhydrous DMF (6 ml) was then added to the red solution of the anion. After stirring for 4 h at 40 °C, the reaction mixture was poured on to ice (40 ml) to give a yellow solid which was collected, washed with water, and identified as the practically pure compound (0·940 g, 5·07 mmol, 47·8%), m.p. 106–108 °C (after sublimation) (found: C, 71·4; H, 6·3; N, 23·0. Calc. for $C_{11}H_{11}N_3$: C, 71·3; H, 6·0; N, 22·7%); δ_H ($CDCl_3$) 8·56 (1 H, d, 6-H), 8·06 (1 H, d, $J_{2,5}$ 1·1, 2-H), 7·84 (1 H, d, $J_{\alpha,\beta}$ 15·6, α-H), 7·12 (1 H, dd, $J_{5,6}$ 5·3, 5-H), 6·74 (1 H, d, β-H), 6·73 (1 H, dd, $J_{4',5'}$ 1·9, 5′-H), 6·68 (1 H, dd, $J_{3',5'}$ 1·6, 3′-H), 6·18 (1 H, dd, $J_{3',4'}$ 3·9, 4′-H), 3·75 (3 H, s, N-Me).

1-(Pyridin-4-yl)-2-(thien-2-yl)ethene (9). A suspension of sodium hydride in oil (60% by weight; 0·47 g corresponding to 0·28 g, 11·8 mmol) was thoroughly washed with anhydrous THF and finally suspended in THF (20 ml). To this suspension, kept under nitrogen, was first added a solution of diethyl 2-thienylmethylphosphonate (2·53 g, 10·8 mmol) in THF (5 ml) and then a solution of 2-thienylcarbaldehyde (1·16 g, 10·8 mmol) in the same solvent (5 ml). The mixture was cautiously heated on an oil-bath at 50 °C until the evolution of hydrogen had ceased, and then at reflux for 1 h. The mixture was poured on to ice (100 ml) to give a yellow solid which was collected, washed with water and identified as the pure product (1·15 g, 6·14 mmol, 56·9%), m.p. 141–143 °C (PhH) (found: C, 70·8; H, 4·5; N, 7·2. Calc. for $C_{11}H_9NS$: C, 70·6; H, 4·8; N, 7·5%); δ_H ($CDCl_3$) 8·54 (2 H,

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d, $J_{2,3}$ 4·6, 2-H and 6-H), 7·41 (1 H, d, $J_{\alpha,\beta}$ 16·1, α-H), 7·29 (2 H, d, 3-H and 5-H), 7·27 (1 H, d, $J_{4',5'}$ 5·1, 5′-H), 7·14 (1 H, d, $J_{3',4'}$ 3·7, 3′-H), 7·20 (1 H, dd, 4′-H), 6·81 (1 H, d, β-H).

*1-(*N*-Methyl-4-pyridinio)-2-(*N*-methylpyrrol-2-yl) ethene triflate (10).* Methyl triflate (0·09 g, 0·54 mmol) in dry benzene (2 ml) was added dropwise at room temperature to a stirred solution of 1-(pyridin-4-yl)-2-(*N*-methylpyrrol-2-yl)ethene (0·10 g, 0·54 mmol) in the same solvent (5 ml). After 1 h the resulting orange precipitate was collected, washed with benzene to give the product (0·16 g, 0·46 mmol, 84·7%), m.p. >240 °C (H_2O) (found: C, 48·4; H, 4·2; N, 8·2. Calc. for $C_{14}H_{15}F_3N_2O_3S$: C, 48·3; H, 4·3; N, 8·0%); δ_H (DMSO-d_6) 8·68 (2 H, d, $J_{2,3}$ 6,7, 2-H and 6-H), 8·10 (2 H, d, 3-H and 5-H), 7·90 (1 H, d, $J_{\alpha,\beta}$ 15·9, α-H), 7·09 (1 H, d, $J_{4',5'}$ 2·0, 5′-H), 7·05 (1 H, d, β-H), 6·88 (1 H, d, $J_{3',4'}$ 3·9, 3′-H), 6·21 (1 H, dd, 4′-H), 4·15 (3 H, s, N^+-Me), 3·80 (3 H, s, N-Me).

1-(N-Cetyl-4-pyridinio)-2-(N-methylpyrrol-2-yl)ethene triflate (11). Cetyl triflate (0·41 g, 1·08 mmol) in dry benzene (5 ml) was dropwise added at room temperature to a stirred solution of 1-(pyridin-4-yl)-2-(*N*-methylpyrrol-2-yl)ethene (0·20 g, 1·08 mmol) in the same solvent (10 ml). After 2 h the resulting orange precipitate was collected and washed with benzene to give the product (0·31 g, 0·55 mmol, 51·4%), m.p. 117 °C (*i*-PrOH) (found: C, 62·2; H, 8·1; N, 5·2. Calc. for $C_{29}H_{45}F_3N_2O_3S$: C, 62·3; H, 8·1; N, 5·0%); δ_H (DMSO-d_6) 8·79 (2 H, d, $J_{2,3}$ 6·6, 2-H and 6-H), 8·13 (2 H, d, 3-H and 5-H), 7·94 (1 H, d, $J_{\alpha,\beta}$ 15·9, α-H), 7·12 (1 H, d, $J_{4',5'}$ 2·8, 5′-H), 7·12 (1 H, d, β-H), 6·90 (1 H, d, $J_{3',4'}$ 3·9, 3′-H), 6·23 (1 H, dd, 4′-H), 4·41 (2 H, t, *J* 7·5, N^+-C<u>H</u>$_2$CH$_2$–), 3·80 (3 H, s, *N*-Me), 1·89 (2 H, m, N^+–CH$_2$C<u>H</u>$_2$–), 1·35–1·18 (26 H, m, —(C<u>H</u>$_2$)$_{13}$—), 0·85 (3 H, t, *J* 6·5, N^+-(CH$_2$)$_{15}$C<u>H</u>$_3$).

1-(N-Methyl-2-pyridinio)-(N-methylpyrrol-2-yl) ethene triflate (12). Methyl triflate (0·09 g, 0·54 mmol) in dry benzene (2 ml) was dropwise added at room temperature to a stirred solution of 1-(pyridin-2-yl)-2-(*N*-methylpyrrol-2-yl)ethene (0·10 g, 0·54 mmol) in the same solvent (5 ml). After 1 h the resulting orange precipitate was collected and washed with benzene to give the product (0·14 g, 0·40 mmol, 74·4%), m.p. 187–188 °C (EtOH) (found: C, 48·1; H, 4·3; N, 8·3. Calc. for $C_{14}H_{15}F_3N_2O_3S$: C, 48·3; H, 4·3; N, 8·0%); δ_H (DMSO-d_6) 8·72 (1 H, d, $J_{5,6}$ 5·8, 6-H), 8·55 (1 H, d, $J_{3,4}$ 6·8 3-H), 8·34 (1 H, t, 5-H), 7·88 (1 H, d, $J_{\alpha,\beta}$ 15·7, α-H), 7·69 (1 H, t, 4-H), 7·13 (1 H, dd, $J_{4',5'}$ 2·5, 5′-H), 7·11 (1 H, d, β-H), 7·08 (1 H, dd, $J_{3',5'}$ 1·7, 3′-H), 6·24 (1 H, dd, $J_{3',4'}$ 4·2, 4′-H), 4·24 (3 H, s, N^+-Me) 3·81 (3 H, s, N-Me).

1-(N-Methyl-4-pyridinio)-2-(thien-2-yl)ethene triflate (13). Methyl triflate (0·09 g, 0·53 mmol) was added at room temperature to a stirred solution of 1-(pyridin-4-yl)-2-(thien-2-yl)ethene (0·10 g, 0·53 mmol) in dry acetone (5 ml). After stirring for 5 h at room temperature the solvent was evaporated to give the product as a yellow solid (0·12 g, 0·34 mmol, 64·4%), m.p. 170–172 °C (*i*-PrOH) (found: C, 44·6; H, 3·5; N, 3·8. Calc. for $C_{13}H_{12}F_3NO_3S_2$: C, 44·4; H, 3·4; N, 4·0%); δ_H (DMSO-d_6) 8·88 (2 H, d, $J_{2,3}$ 6,3, 2-H and 6-H), 8·20 (1 H, d, $J_{\alpha,\beta}$ 15·8, α-H), 8·18 (2 H, d, 3-H and 5-H), 7·79 (1 H, d, $J_{4',5'}$ 4·9, 5′-H), 7·50 (1 H, d, $J_{3',4'}$ 3·6, 3′-H), 7·21 (1 H, dd, 4′-H), 7·18 (1 H, d, β-H), 4·20 (3 H, s, N^+-Me).

1-(Pyridin-4-yl)-1-cyano-2-(N-methylpyrrol-2-yl) ethene (14). Potassium *tert*-butoxide (1·12 g, 9·16 mmol) was added to a solution of 4-pyridylacetonitrile (1·08 g, 9·16 mmol) in *tert*-butanol (10 ml). After stirring for 10 min at room temperature, a solution of *N*-methylpyrrole-2-carboxyaldehyde (1·00 g, 9·16 mmol) in the same solvent (10 ml) was added dropwise to the red solution of the anion. The immediate formation of a yellow precipitate was observed. After 1 h of stirring at room temperature, the solid was collected to afford the practically pure compound (1·57 g, 7·50 mmol, 81·9%), m.p. 186–187 °C (EtOH) (found: C, 74·4; H, 5·1; N, 20·0. Calc. for $C_{13}H_{11}N_3$: C, 74·6; H, 5·3; N, 20·1%); δ_H ($CDCl_3$) 8·60 (2 H, d, $J_{2,3}$ 6·1, 2-H and 6-H), 7·60 (1 H, d, $J_{5',4'}$ 4·4, 5′-H), 7·47 (2 H, d, 3-H and 5-H), 7·34 (1 H, s, β-H), 6·89 (1 H, d, $J_{3',4'}$ 1·9, 3′-H), 6·34 (1 H, dd, 4′-H), 3·77 (3 H, s, N-Me).

1-(Pyridin-4-yl)-1-cyano-2-(N-methylindol-3-yl) ethene (15). Potassium *tert*-butoxide (0·35 g, 3·14 mmol) was added to a solution of 4-pyridylacetonitrile (0·37 g, 3·14 mmol) in *tert*-butanol (5 ml). After stirring for 10 min at room temperature, a solution of *N*-methylindole-3-carboxyaldehyde (0·50 g, 3·14 mmol) in the same solvent (10 ml) was added dropwise to the red solution of the anion. The immediate formation of a light yellow precipitate was observed. After refluxing for 1 h, the solid was collected to afford the practically pure compound (0·65 g, 2·51 mmol, 79·8%), m.p. 210–211 °C (toluene) (found: C, 78·5; H, 5·1; N, 16·0. Calc. for $C_{17}H_{13}N_3$: C, 78·7; H, 5·05; N, 16·2%); δ_H (DMSO-d_6) 8·63 (2 H, d, $J_{2,3}$ 5·5, 2-H and 6-H), 8·54 (1 H, s, 2-H or β-H), 8·48 (1 H, s, 2′-H or β-H), 8·18 (1 H, d, $J_{4',5'}$ 8·1, 4′-H), 7·77 (2 H, d, 3-H and 5-H), 7·61 (1 H, d, $J_{7',6'}$ 8·0, 7′-H), 7·34 (1 H, t, 5′-H), 7·28 (1 H, t, 6′-H), 3·96 (3 H, s, N-Me).

1-(Pyridin-2-yl)-I-cyano-2-(N-methylindol-3-yl)ethene (16). Potassium *tert*-butoxide (0·35 g, 3·14 mmol) was added to a solution of 2-pyridylacetonitrile (0·37 g, 3·14 mmol) in *tert*-butanol (10 ml). After stirring for 10 min at room temperature, a solution of *N*-methylindole-3-carboxyaldehyde (0·50 g, 3·14 mmol) in the same solvent (10 ml) was added dropwise to the red solution of the anion. The immediate formation of a light yellow precipitate was observed. After refluxing for 1 h, the solid was collected to afford the practically pure compound (0·67 g, 2·58 mmol, 82·3%), m.p. 178–179 °C (MeOH) (found: C, 78·9; H, 5·3; N, 16·3. Calc. for $C_{17}H_{13}N_3$: C, 78·7; H, 5·05; N, 16·2%); δ_H ($CDCl_3$) 8·82 (1 H, s, 2′-H or β-H), 8·61 (1 H, d, $J_{6,5}$ 4·9, 6-H), 8·42 (1 H, s, 2-H or β-H), 7·93 (1 H, d, *J* 7·5, aromatic

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H-atom), 7·74 (1 H, td, *J* 6·3, 2·0, aromatic H-atom), 7·65 (1 H, d, *J* 7·8, aromatic H-atom), 7·16–7·41 (4 H, m, aromatic H-atoms), 3·90 (3 H, s, N-Me).

*1-(*N*-Methyl-4-pyridinio)-1-cyano-2-(*N*-methylpyrrol-2-yl)ethene triflate (17).* Methyltriflate (0·23 g, 1·43 mmol) was added at room temperature to a stirred solution of 1-(pyridin-4-yl) -1 - cyano - 2 - (*N* - methylpyrrol - 2-yl)ethene (0·30 g, 1·43 mmol) in dry acetone (10 ml). After 10 h the resulting orange precipitate was collected and washed with acetone to give the product (0·36 g, 0·96 mmol, 67·4%), m.p. 239–240 °C (*i*-PrOH) (found: C, 48·1; H, 3·9; N, 11·15. Calc. for $C_{15}H_{14}F_3N_3O_3S$: C, 48·3; H, 3·8; N, 11·25%); δ_H (DMSO-d_6) 8·83 (2 H, d, $J_{2,3}$ 6·9, 2-H and 6-H), 8·31 (1 H, s, *β*-H), 8·27 (2 H, d, 3-H and 5-H), 7·65 (1 H, d, $J_{4',5'}$ 4·2, 5′-H), 7·51 (1 H, d, $J_{3',4'}$ 2·4, 3′-H), 6·51 (1 H, dd, 4′-H), 4·20 (3 H, s, N^+-Me), 3·93 (3 H, s, N-Me).

*1-(*N*-Methyl-4-pyridinio)-1-cyano-2-(*N*-methylindol-3-yl)ethene triflate (18).* Methyl triflate (0·19 g, 1·157 mmol) in dry benzene (4 ml) was dropwise added to a stirred suspension of 1-(pyridin-4-yl)-1-cyano-2-(*N*-methylindol-3-yl)ethene (0·30 g, 1·157 mmol) in the same solvent (16 ml). The mixture was refluxed for 15 min. After stirring for 3 h at room temperature, the resulting orange precipitate was collected and washed with benzene to give the compound (0·46 g, 1·08 mmol, 93·9%), m.p. >240 °C (MeOH) (found: C, 53·8; H, 4·0; N, 9·8. Calc. for $C_{19}H_{16}F_3N_3O_3S$: C, 53·9; H, 3·8; N, 9·9%) δ_H (DMSO-d_6) 8·92 (1 H, d, $J_{1',\beta}$ 2·0, 2-H or *β*-H), 8·84 (2 H, dd, $J_{2,3}$ 7·1, $J_{2,5}$ 1·7, 2-H and 6-H), 8·71 (1 H, d, 2′-H or *β*-H), 8·35 (2 H, dd, 3-H and 5-H), 8·24–8·30 (1 H, m, aromatic H-atom), 7·64–7·69 (1 H, m, aromatic H-atom), 7·54–7·44 (2 H, m, aromatic H-atoms), 4·25 (3 H, s, N^+-Me), 4·13 (3 H, s, N-Me).

(NOTE ADDED IN PROOF)

The recent report in this Journal by Wilk[39] that some pyridinium surfactants undergo a photostimulated dimerization at the level of the olefinic double bond, prompted us to check the stability of the compounds reported herein. Indeed we found that some of the reported systems undergo a dimerization involving the central ethylenic unit. The transformation is apparently photostimulated since solutions kept in the dark are appreciably more stable and occurs for solutions of the compounds either in $CHCl_3$ or DMSO. The *N*-alkylazinium salts dimerize also in the solid state. This process, very slow for the *N*-methylazinium systems **10** and **12**, takes place in a few days with the *N*-cetylpyridinium salt **11**. Products were identified on the basis of their ^{1}H NMR and UV-Vis spectra. We found that compound **11** in the solid state after one week originates, of the four possible isomeric structures, only two dimers—probably the *syn*-head-to-tail (*syn*-HT) and *syn*-head-to-head (*syn*-HH). ^{1}H NMR spectra (300 MHz, $CDCl_3$), using the pyridine protons as a reference, indicate the molar distribution of **11** (61%), *syn*-HT (36%) and *syn*-HH (3%).

All this is in line with the known fact that a number of olefins can undergo a photochemical four-center cyclomerization when irradiated in the crystalline state. The most important example is the photodimerization of *trans*-cinnamic acid and of some of its derivatives.[40] More recently, the behaviour of styrylpyrilium tetrafluoborate[41] and triflate[42] has been reported in [2+2] cycloadditions.

REFERENCES

1. (a) J. Sandström, Static and dynamic stereochemistry of push-pull and strained ethylenes, in *Top. Stereochem.*, edited by N. C. Allinger, E. L. Eliel and S. H. Wilen, vol. 14, pp. 83–181, Wiley, New York (1983); (b) G. Isaksson and J. Sandström, *Acta. Chem. Scand.*, **27**, 1183 (1973).
2. J. Sandström and I. Wennerbeck, *J. Chem. Soc., Chem. Commun.* 1087 (1971).
3. (a) D. S. Chemla and J. Zyss (Eds), *Nonlinear Optical Properties of Organic Molecules and Crystals*, Vols 1 and 2. Academic Press, New York (1986); (b) P. N. Prasad and J. Williams, *Introduction to Nonlinear Optical Effects in Molecules and Polymers.* Wiley, New York (1971); (c) S. R. Marder, J. E. Sohn and G. D. Stucky (Eds), *Materials for Nonlinear Optics: Chemical Perspectives*, ACS Symposium Series, No. **455**, American Chemical Society, Washington, DC, (1991); (d) G. Zerbi, M. Gussoni and C. Castiglioni, *Conj. Polym.* **99**, 435 (1991).
4. L. T. Cheng, W. Tam, S. H. Stevenson, G. R. Meredith, G. Rikken and S. R. Marder, *J. Phys. Chem.* **95**, 10631 (1991).
5. (a) J. L. Oudar, *J. Chem. Phys.* **67**, 446 (1977); (b) A. Dulcic, C. Flytzanis, C. L. Tang, D Pépin, M. Fétizon and Y. Hoppilliard, *J. Chem. Phys.* **74**, 1559 (1981).
6. (a) R. G. Meredith, D. J. Williams, S. N. Fishman, E. S. Goldbert and U. Z. Kronganz, *J. Phys. Chem.* **87**, 1697 (1983); (b) B. F. Levine, C. G. Bethea, E. Wasserman and L. Leenders, *J. Chem. Phys.* **68**, 5042 (1978); (c) A. Dulcic and C. Flytzanis, *Opt. Commun.* **25**, 402 (1978).
7. M. Blanchard-Desce, J.-M. Lehn, I. Ledoux and J. Zyss, in *Organic Materials for Non-linear Optics*, edited by R. A. Hann and D. Bloor, Special Publication No. 69, p. 170. Royal Society of Chemistry, London (1988).
8. H. Pan, X. Gao, Y. Zhang, P. N. Prasad, B. Reinhardt and R. Kannan, *Chem. Mater.* **7**, 816 (1995).
9. S. Bradamante and G. A. Pagani, *Pure Appl. Chem.* **61**, 709 (1989).
10. A. Berlin, S. Bradamante and R. Ferraccioli, *J. Chem. Soc., Perkin Trans. 2* 1525 (1988).
11. A. Abbotto, V. Alanzo, S. Bradamante and G. A. Pagani, *J. Chem. Soc., Perkin Trans. 2* 481 (1991).
12. S. Bradamante and G. A. Pagani, *J. Chem. Soc., Perkin Trans. 2* 1035 (1987).
13. E. Barchiesi, S. Bradamante and G. A. Pagani, *J. Chem. Soc., Perkin Trans. 2* 1091 (1986).
14. A. R. Katritzky, *Handbook of Heterocyclic Chemistry*, p. 11. Pergamon Press, Oxford (1983).
15. M. Charton, *Prog. Phys. Org. Chem.* **13**, 119 (1981).
16. (a) D. D. Cunningham, L. Laguren-Davidson, H. B. J. Mark, C. V. Pham and H. Zimmer, *J. Chem. Soc., Chem. Commun.* 1021 (1987); (b) A. F. Diaz, J. Crowley, J. Bargon, G. P. Gardini and J. B. Torrance, *J. Electroanal. Chem.* **121**, 355 (1981); (c) G. P. Gardini, *Adv. Heterocycl. Chem.* **15**, 67 (1973); (d) G. Zotti, G.

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Schiavon, N. Comisso, A. Berlin and G. Pagani, *Makromol. Chem.* **36**, 337 (1990); (e) G. Zotti, G. Shiavon, A. Berlin and G. Pagani, *Synth. Met.* **40**, 299 (1991).
17. F. M. Hamer, The Cyanine Dyes and Related Compounds, in *The Chemistry of Heterocyclic Compounds*, edited by A. Weissberger. Wiley, New York (1964) vol. 18.
18. L. Berlin and O. Reister, *Houben-Weyl, Methoden der Organiscen Chemie*, 4th ed., Vol. V/1d, pp. 227–246. Georg Thieme, Stuttgart (1972).
19. D. J. Fry, in *Rodd's Chemistry of Carbon Compounds*, edited by S. Coffey, Vol. 4 (B), p. 370. Elsevier, Oxford (1977).
20. (a) L. G. S. Brooker and R. H. Spague, *J. Am. Chem. Soc.* **67**, 1869 (1945); (b) L. G. S. Brooker, A. L. Sklar, H. W. J. Cressman, G. H. Keyes, L. A. Smith, R. H. Spague, E. Van Lare, G. Van Zandt, F. L. White and W. W. Williams, *J. Am. Chem. Soc*. **67**, 1875 (1945); (c) L. G. S. Brooker, R. H. Spague and H. W. J. Cressman, *J. Am. Chem. Soc.* **67**, 1889 (1945).
21. J. F. Nicoud and R. J. Twieg, in *Nonlinear Optical Properties of Organic Molecules and Crystals*, edited by D. S. Chemla and J. Zyss, Vol. 1, p. 227. Academic Press, New York (1986).
22. C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed. VCH, Weinheim (1988).
23. C. Srinivasan, A. Shanmugasundaram, H. Gunther and N. Finneiser, *Indian J. Chem.* **30B**, 966 (1991).
24. (a) S. Bradamante and G. A. Pagani, *J. Org. Chem.* **49**, 2863 (1984); (b) E. Barchiesi, S. Bradamante, R. Ferraccioli and G. A. Pagani, *J. Chem. Soc., Perkin Trans. 2* 375 (1990), and references cited therein.
25. (a) A. Abbotto, V. Alanzo, S. Bradamante and G. A. Pagani, *J. Chem. Soc., Perkin Trans. 2* 481 (1991); (b) E. Barchiesi and S. Bradamante, *J. Phys. Org. Chem.* **3**, 139 (1990); (c) C. Gatti, A. Ponti, A. Gamba and G. Pagani, *J. Am. Chem. Soc.* **114**, 8634 (1992).
26. G. S. He, L. Yuan, P. N. Prasad, A. Abbotto, A. Facchetti and G. A. Pagani, *Opt. Commun.* 1997, in press.
27. E. Hertel and H. Luhrmann, *Z. Phys. Chem. Abt. B* **44**, 261 (1939).
28. G. P. Schiemenz and M. Finzenhagen, *Liebigs Ann. Chem.*, 1476 (1981).
29. G. Favini, *Gazz. Chim. Ital*. **93**, 635 (1963).
30. A. P. Phillips, *J. Org. Chem.* **12**, 333 (1947).
31. H.-H. Perkampus, T. Bluhm and J. W. Knop, *Spectrochim. Acta, Part A* **28**, 2163 (1972).
32. H.-O. Kalinowski, S. Berger and S. Braun, *Carbon-13 NMR Spectroscopy.* Wiley, New York (1988).
33. H.-P. Erb and T. Bluhm, *Org. Magn. Reson.* **14**, 285 (1980).
34. (a) J. Moir, *J. Chem. Soc.* **127**, 2338 (1925); (b) *UV Atlas of Organic Compounds*, Vol. 4. Verlag Chemie, Weinheim (1968).
35. M. Witanowski, L. Stefaniak and G. A. Webb, *Ann. Rep. NMR Spectrosc.* **18**, 495 (1986).
36. A. Abbotto, S. Bradamante and G. A. Pagani, *J. Org. Chem.* **61**, 1761 (1996).
37. A. Facchetti and G. A. Pagani, to be submitted.
38. R. M. Kellogg, M. B. Groen and H. Wynberg, *J. Org. Chem.* **32**, 3093 (1967).
39. T. Koźlecki and K. A. Wilk, *J. Phys. Org. Chem.* **9**, 645 (1996).
40. (a) M. D. Cohen and G. M. Schmidt, *J. Chem. Soc.*, 1996 (1964); (b) M. D. Cohen, G. M. Schmidt and F. I. Sonntag, *J. Chem. Soc.*, 2000 (1964).
41. K. Hense and S. Hunig, *Liebigs Ann. Chem.*, 715 (1985).
42. K. Novak, V. Enkelmann, W. Kohler, G. Wegner and K. B. Wagener, *Mol. Cryst. Liq. Crist.* **242**, 269 (1994).

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