Synthesis, spectroscopic studies and structural characterisation of some new 2-(phosphonioaryl)imidazolide betaines

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The synthesis is described of three series of 2-(phosphonioaryl)(benz)imidazolide betaines, *viz* (i) the 2-(2- or 3- or 4-tributylphosphoniophenyl)benzimidazolides, (ii) the 2-(2- and 4-triorganophosphoniophenyl)-1*H*-phenanthro[9,10-*d*]imidazolides, and (iii) the 2-(2- and 4-triorganophosphoniophenyl)-4,5-diphenylimidazolides. A detailed ¹H, ¹³C and ³¹P NMR study of the 2-(tributylphosphoniophenyl)benzimidazolides reveals significant differences in the spectroscopic parameters of the betaines compared with those of the phosphonium salts from which they are derived. Full X-ray structural studies are reported for 2-(4-triphenylphosphoniophenyl)-1*H*-phenanthro[9,10-*d*]imidazol-1-ide and 2-(4-triphenylphosphoniophenyl)-4,5-diphenylimidazol-1-ide, and comparisons made with related pyridiniumimidazolide systems. The phosphonioimidazolide betaines exhibit negative solvatochromism.

Introduction

A recent theoretical study[1] has highlighted a new approach to the design of second order non-linear optical (NLO) materials, based on a family of dipolar heterocyclic betaines, *e.g.* **1**, the synthesis of which has been explored by Alcalde *et al.*[2] and which offer the possibility of short-range charge-transfer from a charged aromatic electron donor to a directly-linked, charged aromatic acceptor group, which gives rise to a large difference between the dipole moments of the excited and ground state molecules. These systems are different to conventional 'push–pull' systems, *e.g.* 'DANS' **2** in which long range charge-transfer
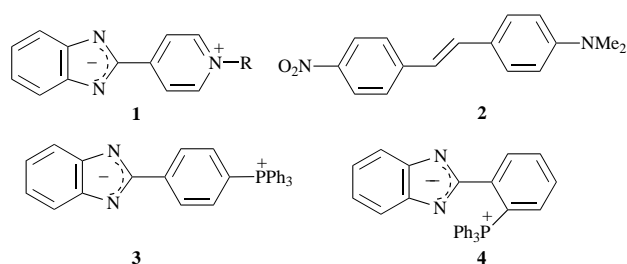

occurs from a non-aromatic donor to a non-aromatic acceptor, through a π-delocalised electron bridge. Extremely large molecular hyperpolarisabilities have been predicted for the above heterocyclic betaines and such systems appear to have considerable potential for NLO applications.

Recently[3] we have investigated the alkaline hydrolysis products of a series of arylphosphonium salts bearing benzimidazolyl substituents in the aryl ring attached to phosphorus. Treatment of these salts with one equivalent of aqueous sodium hydroxide generated the corresponding stable phosphonium benzimidazolide betaines **3** and **4** which were fully characterised.

Although the possibility of mesomeric intramolecular charge-transfer in these phosphonium betaines is reduced compared to the pyridinium system **1**, as a result of the now recognised reluctance of phosphorus to become involved in d_π-bonding,[4] compounds of this type are nevertheless still of interest as potential NLO systems as the π-electron system will be perturbed by inductive and/or field effects by the phosphonium

centre, as has been pointed out for a series of organoammonium organoborate zwitterions **5** in which the positive and negative centres are separated by a polarisable π-system.[5] Due to the current interest in organic substrates with high dipole moments, we have extended our study and now describe the synthesis and characterisation of a wider range of related phosphonium systems, together with a full structural characterisation of two representative compounds by X-ray techniques.

Three series of compounds have been prepared: (i) the 2-tributylphosphoniophenyl)benzimidazolide system **6**; (ii) the 2-
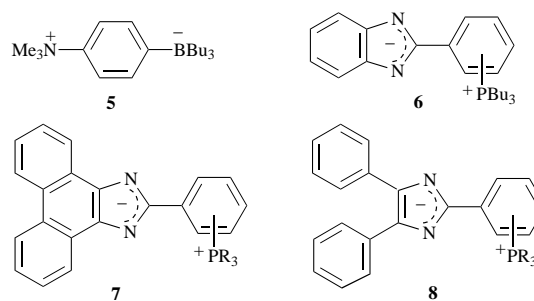

phosphoniophenyl-1*H*-phenanthro[9,10-*d*]imidazolides (**7**; R = Ph or Bu); (iii) the 2-phosphoniophenyl-4,5-diphenylimidazolides (**8**; R = Ph or Bu).

Results and discussion

The synthetic route (Scheme 1) to this series of betaines begins with the synthesis of the required 2-(bromophenyl)imidazoles using established general procedures[6,7] in yields of 50–75%. The bromoarene was then converted into the required arylphosphonium salt by the Horner method[8] *via* treatment with the appropriate tertiary phosphine and nickel(II) bromide, in benzonitrile under reflux. The salt was isolated by pouring the reaction mixture into a solution of potassium bromide followed by an extraction using dichloromethane. Trituration with diethyl ether afforded the relatively pure product, in yields ranging from 60 to 90%.

Treatment of the salt with an equimolar proportion of aqueous sodium hydroxide in ethanol or methanol (depending
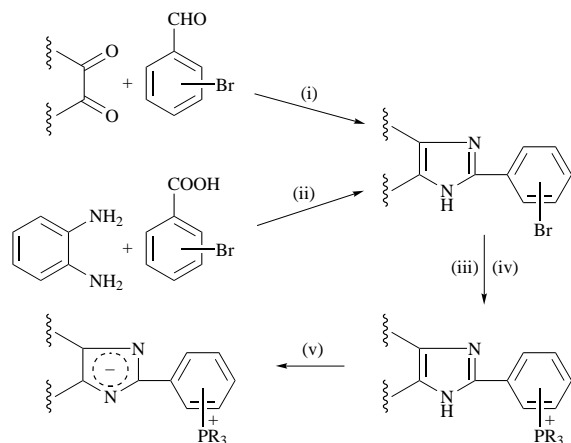
Scheme 1 *Reagents and conditions*: (i) NH$_4$OAc–HOAc, reflux; (ii) PPA, 180–200 °C; (iii) R$_3$P, NiBr$_2$–PhCN, reflux under N$_2$; (iv) aq. KBr; (v) NaOH (1 mol equiv.)

on the solubility of the phosphonium salt) gave the corresponding stable phosphonium betaine in good yield (80–95%). Most of the betaines crystallised out of solution, but some required further dilution of the reaction mixture with water. The 2-(2-tributylphosphoniophenyl)-1*H*-benzimidazolide betaine **6** was an oil and was extracted from the reaction mixture using dichloromethane, and subsequently purified by trituration with diethyl ether.

Although the synthetic routes to the phosphonium betaines were fairly straightforward, difficulties did, however, arise with the purification of many of the intermediate phosphonium salts, which were often oily or hygroscopic. This problem was overcome by converting them to the related perchlorate salt, giving pure products with good microanalytical agreement. Microanalytical and NMR spectroscopic data and, in two cases, X-ray structure analysis for the betaines were consistent with the betaine formulation although all strongly retained molecules of polar solvents *e.g.* ethanol or water on recrystallisation. This phenomenon has also previously been noted with the series of related pyridinium betaines described by Alcalde *et al.*[2] All the betaines synthesised gave a negative halide test on treatment with aqueous silver nitrate in aqueous ethanol (or methanol) acidified with dilute nitric acid, whereas the parent phosphonium salts readily gave a precipitate of silver bromide.

The ability of these phosphonium betaines to act as nucleophiles has been investigated by their reactions with a reactive benzyl halide. Refluxing the phosphonium betaine with an equimolar proportion of 4-nitrobenzyl bromide in dry acetonitrile or dimethylformamide resulted in the formation of the corresponding *N*-(4-nitrobenzyl)imidazole derivative (Scheme 2). A few reactions of this type were also carried out using
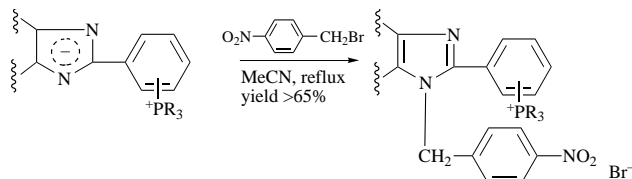
Scheme 2

iodomethane. However, although the desired products were obtained, the yields were poor in comparison, possibly due to the volatility of the iodomethane under the conditions used.

In our earlier paper,[3] it was reported that ^{31}P NMR studies on the triphenylphosphoniobenzimidazolide betaines **3** and **4** showed that for the *ortho*-isomer **4**, the phosphorus nucleus is significantly shielded ($\delta = -14.7$ ppm in deuteriochloroform) relative to that of the parent salt ($\delta = 25.3$ ppm). In contrast, for the *para*-isomer **3**, both betaine and salt have virtually identical chemical shifts (22.6 and 23.0 ppm, respectively). This suggests
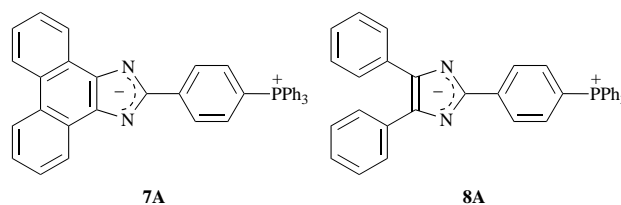
that in the *ortho*-isomer, there is an interaction between the phosphonium centre and the benzimidazolide system, thus tending towards a phosphorane-like species. We have now studied this interaction by variable temperature ^{31}P NMR and find that on progressively cooling the sample, the ^{31}P signal broadens and gradually moves to lower field but never resolves into two discrete signals. Similar *ortho*-effects are also observed with the new phosphoniophenylimidazolide betaines described in this paper. However it is evident that the *ortho*-shift in these compounds is less pronounced than those described earlier. This may perhaps be attributed to the electronic effects of the tributylphosphonio group compared to triphenylphosphonio at the cationic centre, and in **7** and **8**, greater delocalisation of negative charge over the imidazolide centre, thus weakening the interaction with the phosphonium ion. This effect is clearly impossible in the related *meta*- and *para*-betaines, and as expected, the ^{31}P chemical shifts of these betaines were little different to those of the parent salts. It was also noted that protonation of the betaines using trifluoroacetic acid moved the ^{31}P signal to that observed when trifluoroacetic acid is added to a solution of the parent salt in deuteriochloroform.

Discussion of structural data

Full X-ray structural studies of two representative members of the series of phosphoniumbenzimidazolide betaines have been carried out.† The observed structures of **7A** and **8A** are dis-

played in Figs. 1 and 2, respectively, and confirm their betaine nature. Halide ions were not detected in the crystallographic study. Selected bond lengths for **7A** and **8A** are given in Table 1. In general, bond lengths within the imidazolide unit are very similar to those reported by Alcalde *et al.*[9] for related *N*-alkylpyridiniumbenzimidazolide betaines, and, in any event, are very similar to those reported in benzimidazole itself.[10] Bond angles about phosphorus are very close to those expected for a tetrahedral phosphonium unit. The interannular bond between the imidazolide unit and the ring bearing the phosphonium group appears to be essentially a single bond in both compounds, implying little conjugative interaction between the charged centres. However, the torsional angle between the heterocyclic ring and the benzene ring bearing the phosphonium group in **7A** was found to be 18.9°, and only 10.4° in **8A**, possibly implying some attempt to achieve p$_\pi$-orbital overlap through the system. There is no evidence of any bond shortening between the phosphonium centre and the benzene ring bearing the imidazolide moiety. Both phosphonium betaines are

Table 1 Selected bond lengths in compounds **7A** and **8A** (Å)

Compound **7A** (contained two independent molecules per unit cell)		Compound **8A**
C25–N1	1.33(2)	1.37(2)	1.407(8)
C25–N2	1.36(2)	1.34(2)	1.349(7)
C22–C25	1.41(2)	1.51(2)	1.471(7)
P1–C19	1.791(14)	1.73(2)	1.821(5)

† Full crystallographic details, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc.*, *Perkin Trans. 1*, available *via* the RSC Web pages (http://www.rsc.org/authors). Any request to the CCDC for this material should quote the full literature citation and the reference number 207/164.
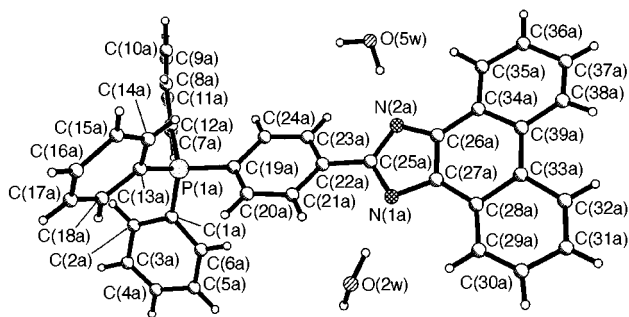
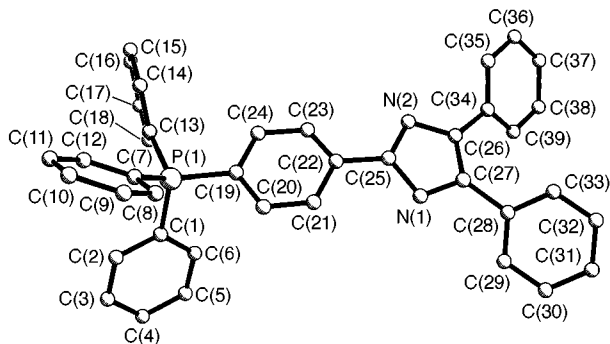**Fig. 1** Molecular structure of 2-(4-triphenylphosphoniophenyl)-1*H*-phenanthro[9,10-*d*]imidazolide **7A**

Fig. 2 Molecular structure of 2-(4-triphenylphosphoniophenyl)-4,5-diphenylimidazolide **8A**
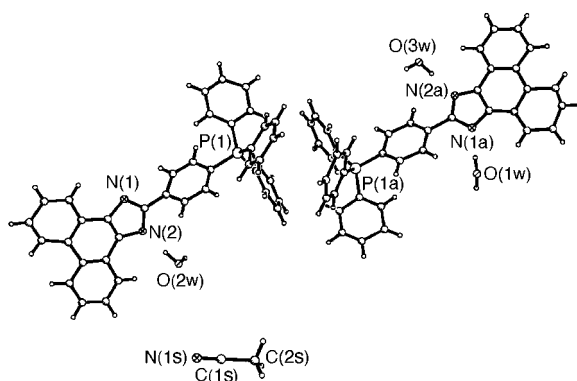

Fig. 3 Association between cationic centres of the betaine **7A** in the solid state

associated with varying numbers of solvent molecules (water and/or ethanol, or acetonitrile, largely associated with both heterocyclic nitrogens), as was the case for the related pyridinium systems. It was noted that in the crystal lattice of **7A**, two molecules appeared to relate to each other in a head to head manner, *via* interactions between the benzene rings of the triphenylphosphonio unit (Fig. 3). Such interactions have been recently recognised as existing in many crystal lattices involving triphenylphosphonio units (as in a variety of tetraphenylphosphonium salts, and triphenylphosphino complexes), and various specific phenyl embrace modes categorised, and shown to be quite significant interactions in energy terms.[11,12] In the case of **7A**, the interaction conforms most closely to a 'translational quadruple phenyl embrace'. In contrast, the molecules of **8A** pack in a head to tail manner, the phenyl rings of the triphenylphosphonio moiety appearing to interact with the phenyl substituents in the 4,5- position of the imidazolide system.

Crystal data for 7A. $C_{78}H_{54}N_4P_2 \cdot 3H_2O \cdot 0.5CH_3CN$, M 1183.77. Crystallises from ethanol–acetonitrile as pale yellow oblongs; crystal dimensions $0.66 \times 0.43 \times 0.21$ mm. Tetragonal, $a = 25.637(5)$, $b = 25.637(5)$, $c = 19.271(7)$ Å, $U = 12\,666(6)$ Å^3, $Z = 8$, $D_c = 1.254$ g cm^{-3}, space group $P\bar{4}\,2_1c$ (No. 114), Mo-Kα radiation ($\lambda = 0.710\,69$ Å), μ(Mo-Kα) = 0.126 cm^{-1}, $F(000) = 4968$.

Three-dimensional, room temperature X-ray data were collected in the range $3.5 < 2\theta < 45°$ on a Siemens P4 diffractometer by the omega scan method. Of the 10 464 reflections measured, all of which were corrected for Lorentz and polarisation effects (but not for absorption), 2687 independent reflections exceeded the significance level $|F|/s(|F|) > 4.0$. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2. A molecule of acetonitrile was found and refined at a 50% occupancy. Hydrogen atoms were included in calculated positions and refined in riding model. Refinement converged at a final $R = 0.0987$ ($wR_2 = 0.3173$, for all 5190 unique data; 800 parameters, mean and maximum d/σ 0.000, 0.000), with allowance for the thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density -0.250 and 1.030 e Å^{-3}. A weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.1413P)^2 + 0.000P]$ where $P = (F_o^2 + 2F_c^2)/3$ was used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXL93[13] as implemented on the Viglen 486dx computer.

Crystal data for 8A. $C_{39}H_{29}N_2P \cdot 0.75C_2H_5OH \cdot 0.2H_2O$; $M = 672.26$. Crystallises from ethanol as pale yellow blocks; crystal dimensions $0.18 \times 0.12 \times 0.10$ mm. Orthorhombic, $a = 12.425(2)$, $b = 15.394(3)$, $c = 19.546(4)$ Å, $U = 1287.2(6)$ Å^3, $Z = 4$, $D_c = 1.194$ g cm^{-3}, space group $P2_12_12_1$ (D_2^4, No. 19), Mo-Kα radiation ($\lambda = 0.710\,73$ Å), μ(Mo-Kα) = 0.116 mm^{-1}, $F(000) = 1426$.

Three-dimensional, low temperature X-ray data were collected in the range $3.5 < 2\theta < 50°$ on a Delft FAST TV area-detector diffractometer by the omega scan method. Of the 14 945 reflections measured, all of which were corrected for Lorentz and polarisation effects (but not for absorption), 1549 independent reflections exceeded the significance level $|F|/s(|F|) > 4.0$. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2. Hydrogen atoms were included in calculated positions and refined in riding model. Refinement converged at a final $R = 0.0493$ ($wR_2 = 0.0961$, for all 5721 unique data; 395 parameters, mean and maximum d/σ 0.000, 0.000), with allowance for the thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density -0.231 and 0.225 e Å^{-3}. A weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0483P)^2 + 0.000P]$ where $P = (F_o^2 + 2F_c^2)/3$ was used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXL93[13] as implemented on the Viglen 486dx computer.

NMR study of the betaines 6 and a comparison with their parent salts

A detailed study of the ^{1}H, ^{13}C and ^{31}P NMR spectra has revealed significant differences in the NMR parameters of the betaines **6** and the parent phosphonium salts, implying that the betaines exist as independent species with an electronic structure which is different to the salts from which they are derived. This study was carried out using a Bruker AMX2-400 spectrometer at 400.13 MHz (^{1}H), 161.97 MHz (^{31}P) and 100.63 MHz (^{13}C). Chemical shifts are reported on the δ scale in ppm and are accurate to two decimal places in the case of ^{1}H spectra and one decimal place for the ^{13}C and ^{31}P spectra. The numbering system used in discussion of the spectra is as follows:
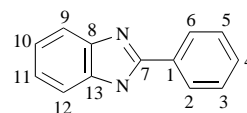
The position of the tributylphosphonium substituent is the key indicator of structure in the tables of data, *e.g.* '3-betaine' has the phosphonium group at position 3 of the phenyl ring. The ^{1}H data are displayed in Table 2, the ^{13}C data in Table 3, and the ^{31}P data in Table 4.

Proton assignments are based on coupling constants and H{P} decoupling experiments. The protons *ortho* to the phos-

Table 2 ^{1}H NMR data for betaines **6** and related phosphonium salts (δ/ppm) (J values are given in Hz)

	2-betaine	2-salt	3-betaine	3-salt	4-betaine	4-salt
H2	—		8.92 $^3J_{PH} = 13.0$ $^4J_{24} = 1.4$ $^4J_{26} = 1.5$	9.55 $^3J_{PH} = 13.2$ $^4J_{24} = 1.5$ $^4J_{26} = 1.5$	7.67 $^4J_{PH} = 2.9$ $\lvert{}^3J_{HH} + {}^5J_{HH}\rvert = 8$ 5	8.67 $^4J_{PH} = 2.6$ $\lvert{}^3J_{HH} + {}^5J_{HH}\rvert = 8$ 6
H3	7.43 $^3J_{PH} = 12.7$ $^3J_{34} = 7.6$ $^4J_{35} = 1.3$	7.76 $^3J_{PH} = 13.3$ $^3J_{34} = 8.0$ $^4J_{35} = 0.2$	—	—	6.93 $^4J_{PH} = 11.4$	7.66 $^4J_{PH} = 11.4$
H4	7.35 $^4J_{PH} = 3.1$ $^3J_{45} = 7.6$ $^4J_{46} = 1.4$	7.60 $^4J_{PH} = 2.5$ $^3J_{45} = 7.4$ $^4J_{46} = 1.2$	7.39 $^3J_{PH} = 11.2$ $^3J_{45} = 7.7$ $^4J_{46} = 1.2$	7.57 $^3J_{PH} = 10.8$ $^3J_{45} = 7.8$ $^4J_{46} = 1.4$		
H5	7.76 $^5J_{PH} = 1.7$ $^3J_{56} = 7.7$	7.76 $^5J_{PH} = 5.6$ $^3J_{56} = 8.1$	7.54 $^4J_{PH} = 1.3$ $^3J_{56} = 7.9$	7.67 $^4J_{PH} = 3.6$ $^3J_{56} = 8.0$		
H6	8.71 $^4J_{PH} = 4.6$	8.84 $^4J_{PH} = 4.8$	8.73	8.77 $^4J_{PH} = 1.4$		
NH		13.72 ν 15 Hz^c		13.2 ν 500 Hz^c		13.3 ν 640 Hz^c
H9/12	7.65	7.89^a 7.65^a	7.64	7.73	7.76^b $^3J_{9,10} = 8.0$ $^4J_{9,11} = 1.2$ $^5J_{9,12} = 0.8$	7.71
H10/11	7.03	7.20	7.03	7.19	6.94^b $^3J_{10,11} = 6.9$ $^4J_{10,12} = 1.2$	7.13
PCH$_2$	2.46	2.64	2.14	2.74	1.74	2.50
β-CH$_2$	1.44	1.41	1.26	1.47	0.96	1.32
γ-CH$_2$	1.32	1.34	1.17	1.45	1.17	
CH$_3$	0.80	0.76	0.75	0.89	0.69	0.77

^{a} Signals broad. ^{b} These values are typical of the couplings found in the benzimidazole ring system. ^{c} Peak width at half-height.

phorus in the phosphonium system were determined using NOE measurements involving irradiating the PCH$_2$ group—in all cases NOE enhancements in excess of 5% were observed.

The proton spectra can be divided into a number of parts: the *n*-butyl groups bonded to the phosphorus, the benzimidazole ring and the phenyl ring bearing the phosphonium system. The salts also have an NH resonance at *ca.* 13.5 ppm.

For both the 3- and the 4-salts, NH exchange between the two nitrogens on the benzimidazole system is relatively fast such that the protons approximate to an [AB]$_2$ spin system. In the 2-salt, NH exchange is relatively slow so that there is no longer a plane of symmetry and two broad resonances are observed for H9 and H12. One possible reason for this relatively slow rate of exchange may be the formation of a ring system involving the NH-C-C-C-P system with the bromide counterion. In the betaines, the benzimidazole protons always appear as an [AB]$_2$ spin system; the clearest example was obtained for the 4-isomer and the spectrum was fully analysed and the typical coupling constants involved are included in the table.

For the protons of the phenyl ring, the assignments depended on determining which protons were *ortho* to the phosphorus—this information was successfully obtained using NOE measurements. Simple decoupling difference experiments then confirmed the coupling between the homonuclear coupling involving the proton *ortho* to the phosphorus and its nearest neighbour. Confirmation of the chemical shifts and coupling constants were obtained using the WIN-DAISY spin simulation program. The proton assignments were then used to assign the carbon-13 data using a standard HMQC experiment.

Carbon-13 chemical shifts have been assigned using the Attached Proton Test and HMQC experiments using proton chemical shift assignments. Some ambiguity may exist in the assignment of the phenylphosphonium ring carbons because of the similarity of chemical shifts and coupling constants.

The carbon-13 spectrum can be divided up into three parts corresponding to the *n*-butyl group, the phenyl ring bearing the phosphonium group, and the benzimidazole ring. In all six compounds studied, the four carbon resonances for the *n*-butyl

chain were sharp with the α, β and γ CH$_2$ groups displaying coupling to the phosphorus. Similarly, the carbon resonances for the phosphonium salt benzene ring were sharp and displayed coupling to phosphorus for all six compounds. The largest differences between the betaines and the salts appear when the resonances of the benzimidazole ring are compared. As expected, the NCN carbon is sharp in all six compounds because NH exchange would not affect its chemical environment. For the betaines there is a plane of symmetry throughout the ring and only three different carbon resonances should be observed; this is observed in practice. For the phosphonium salts, the carbons are all different. How different depends upon the rate of NH exchange. In the 2-salt, all six carbon resonances are observed at room temperature with only a slight line broadening with respect to the phenylphosphonium ring carbons. For the 3- and 4-salts, only one resonance is clearly visible (line width approximately 20 Hz) with a second resonance nearly lost in the baseline noise. Cooling the latter salts down to −50 °C slowed the rate of exchange and all six different resonances were observed even though they had a line width in the region of 20 Hz. Clearly, the rate of NH exchange in the *ortho*-salt is different from that of the other two, and the difference could arise from some interaction with the phosphorus.

The ^{31}P spectrum of all six compounds consists of a single resonance. Only in the case of the 2-phosphoniophenyl systems is there a significant difference in chemical shift, which, as argued above, may indicate some intramolecular interaction between the heterocyclic nitrogen and phosphorus atoms in the betaine. On cooling the sample down to −50 °C, there was no significant change in chemical shift that might indicate a strengthening of such an interaction between the nitrogen and the phosphorus. The chemical shifts of the other systems were also independent of temperature.

Solvatochromism of the betaines
The UV-visible absorption spectra of the betaines and their parent salts also confirm that the betaines are, without doubt, new systems, the electronic structure of which differ signifi-

Table 3 ^{13}C NMR data for betaines **6** and related phosphonium salts (δ/ppm)

	2-betaine	2-salt	3-betaine	3-salt	3-salt at −50 °C	4-betaine	4-salt	4-salt at −50 °C
C-8q	147.1	135.2	143.4	Not visible	134.6^a	146.3	Not visible	134.7^a
C-9H	117.0	118.3	116.2	116 (very broad)	118.6^a	117.1	116 (very broad)	118.5^a
C-10H	119.2	122.6	120.9	122.7 (broad)	122.1^a	119.8	122.8 (broad)	122.3^a
C-11H		124.1			123.2^a			123.2^a
C-12H		113.4			112.4^a			112.3^a
C-13q		142.4		Not visible	142.8^a		Not visible	142.8^a
C-7	157.5	148.4	153.8	149.2	149.0	156.8	149.1	149.0
C-1q	143.7(6)	135.1(5)	136.4(12)	133.2(11)	132.5(12)	142.1(3)	135.9(2)	135.2(0)
C-2	114.2q(87)	115.2q(80)	129.7(10)	130.9(12)	130.4(12)	131.0(9)	131.7(9)	131.7(8)
C-3	132.6(10)	134.4(8)	117.1q(81)	117.2q(81)	117.2(82)	128.2(12)	128.4(12)	127.9(9)
C-4	126.8(12)	130.0(11)	130.0(9)	131.1(9)	131.2(8)	113.2q(82)	117.1q(81)	116.8(80)
C-5H	133.8(2)	134.9(0)	130.2(12)	130.2(12)	130.2(12)			
C-6H	130.3(10)	132.8(2)	132.8(2)	133.1(0)	132.7(0)			
CH$_3$	13.4	13.3	13.3	13.4	13.6	13.4	13.2	13.4
CH$_2$	23.9(17)	23.7(17)	23.4(19)	23.6(15)	23.7(17)	23.4(15)	23.5(15)	23.5(17)
CH$_2$	24.7(4)	24.5(4)	23.3(3)	23.6(3)	23.2(3)	23.3(5)	23.4(4)	23.0(0)
CH$_2$	24.7(55)	22.8(51)	18.7(49)	19.5(48)	18.8(49)	18.7(49)	19.5(49)	18.7(49)

^{a} Peak width at half-height = 20–25 Hz.

Table 4 ^{31}P NMR data for betaines **6** and related phosphonium salts/ppm

2-betaine	2-salt	3-betaine	3-salt	4-betaine	4-salt
24.9	32.2	30.3	31.3	28.2	31.1

Table 5 Solvatochromism of the betaines **3**, **7A** and **8A**

	λ_{max}/nm		
Solvent	3	7A	8A
Methanol	330	376	358
Acetonitrile	382	432	434
Acetone	394	446	452
Dichloromethane	394	446	448
THF	416	472	468

cantly from that of their parent salts. In every case, the absorption maximum of the betaine occurs at significantly longer wavelength than that of the salt. Furthermore, whereas the spectra of the salts showed little variation with change in the solvent, those of the betaines showed significant solvatochromic effects. Thus, *e.g.* the parent salt of the betaine **8A** showed an absorption maximum of 360 nm in acetonitrile, whereas the betaine showed an absorption maximum of 434 nm in the same solvent, the band position moving to 468 nm in THF. Full details of the solvatochromism of the betaines **3**, **7A** and **8A** are presented in Table 5. In each case, the absorption maximum moves to longer wavelength as the polarity of the solvent decreases, displaying negative solvatochromism, consistent with a transition from the dipolar ground state to a less polar excited state, in which the negative charge is displaced towards the cationic centre.

Few solvatochromic phosphonium betaine systems have been described. We have recently reported a series of phosphoniophenolate betaines which also display significant negative solvatochromic properties.[14] The above phosphonioimidazolide betaines exhibit a very similar solvatochromic range to the phosphoniophenolate betaines, but the absorption envelope in the phosphonioimidazolides is shifted further to the shorter wavelength end of the visible region compared to the phosphonium phenolates.

Experimental

General
In the preparative work, ^{31}P and ^{1}H NMR studies were carried out using a Bruker AC 250 FTNMR spectrometer. Mass spectra were recorded on a VG Micromass 7070F instrument. Infrared spectra were recorded as a mull or KBr disc using a Philips PU9706 spectrometer.

2-(Bromophenyl)-1*H*-benzimidazoles were prepared by the general procedure[6] from the related bromobenzoic acid, *o*-phenylenediamine and polyphosphoric acid at 180–200 °C.

Bromoarylimidazoles
Bromoarylimidazoles were prepared by a literature procedure[7] by refluxing the related bromobenzaldehyde and benzil or phenanthrenequinone in the presence of ammonium acetate using glacial acetic acid as the solvent. The following compounds were prepared by this method.

2-(2-Bromophenyl)-4,5-diphenylimidazole. White crystals, mp >250 °C (Found: C, 67.34; H, 4.08; N, 7.45; $C_{21}H_{15}N_2Br$ requires C, 67.21; H, 4.03; N, 7.46%); *m/z* 373.8 and 375.7 base peaks (M$^+$).

2-(3-Bromophenyl)-4,5-diphenylimidazole. White crystals, mp >300 °C (decomp.) (Found: C, 67.44; H, 3.95; N, 7.44; $C_{21}H_{15}N_2Br$ requires C, 67.21; H, 4.03; N, 7.46%); *m/z* FAB 373.9 and 375.9, (M$^+$) base peak 153.6.

2-(4-Bromophenyl)-4,5-diphenylimidazole. White crystals, mp 268–271 °C (Found: C, 67.69; H, 3.99; N, 7.51; $C_{21}H_{15}N_2Br$ requires C, 67.21; H, 4.03; N, 7.46%); *m/z* 373.8 and 375.8 base peaks (M$^+$).

2-(2-Bromophenyl)-1*H*-phenanthro[9,10-*d*]imidazole. Off-white crystals, mp 235–237 °C (Found: C, 67.85; H, 3.63; N, 7.40; $C_{21}H_{13}N_2Br$ requires C, 67.58; H, 3.51; N, 7.51%); *m/z* 371.8 and 373.8 base peaks (M$^+$).

2-(3-Bromophenyl)-1*H*-phenanthro[9,10-*d*]imidazole. White crystals, mp 129–131 °C (Found: C, 67.88; H, 3.53; N, 7.39; $C_{21}H_{13}N_2Br$ requires C, 67.58; H, 3.51; N, 7.51%); *m/z* FAB 371.8 and 373.8 base peaks (M$^+$).

2-(4-Bromophenyl)-1*H*-phenanthro[9,10-*d*]imidazole. White crystals, mp 274–276 °C (Found: C, 67.80; H, 3.61; N, 7.51; $C_{21}H_{13}N_2Br$ requires C, 67.58; H, 3.51; N, 7.51%); *m/z* 371.9 and 373.9 base peaks (M$^+$).

Arylphosphonium salts
Arylphosphonium salts were prepared by the established general procedure from the related bromoarene and tertiary phosphine in the presence of nickel(II) bromide using benzonitrile as the solvent. The following new salts were isolated and characterised.

2-(2-Triphenylphosphoniophenyl)-4,5-diphenylimidazole bromide. Pale yellow solid, characterised as the related *perchlorate*, mp 306–308 °C (Found: C, 71.54; H, 4.63; N, 4.26; $C_{39}H_{30}N_2P\cdot ClO_4$ requires C, 71.29; H, 4.60; N, 4.26%). *Bromide salt*: δ_P(CDCl$_3$) 25.68; *m/z* 556.9 base peak (M$^+$).

2-(3-Triphenylphosphoniophenyl)-4,5-diphenylimidazole bromide. Pale yellow solid, characterised as the related *perchlorate*, mp 159–161 °C (Found: C, 71.39; H, 4.49; N, 4.40; $C_{39}H_{30}N_2P \cdot ClO_4$ requires C, 71.29; H, 4.60; N, 4.26%). *Bromide salt*: $\delta_P(CDCl_3)$ 23.10; m/z 555.9 base peak ($M^+ - 1$, betaine), 556.9 (M^+).

2-(4-Triphenylphosphoniophenyl)-4,5-diphenylimidazole bromide. Pale yellow solid, characterised as the related *perchlorate*, mp 170–172 °C (Found: C, 71.30; H, 4.60; N, 4.26; $C_{39}H_{30}N_2P \cdot ClO_4$ requires C, 71.29; H, 4.60; N, 4.26%). *Bromide salt*: $\delta_P(CDCl_3)$ 22.59; m/z 557.0 base peak (M^+).

2-(2-Triphenylphosphoniophenyl)-1H-phenanthro[9,10-d]imidazole bromide. Yellow crystals, mp >360 °C from dichloromethane–diethyl ether (Found: C, 73.90; H, 4.50; N, 4.43; $C_{39}H_{28}N_2P \cdot Br$ requires C, 73.71; H, 4.44; N, 4.41%); $\delta_P(CDCl_3)$ 26.76; m/z (FAB) 554.7 (M^+).

2-(3-Triphenylphosphoniophenyl)-1H-phenanthro[9,10-d]-imidazole bromide. Yellow solid, characterised as the related *perchlorate*, mp 232–234 °C (Found: C, 71.41; H, 4.31; N, 4.22; $C_{39}H_{28}N_2P \cdot ClO_4$ requires C, 71.51; H, 4.31; N, 4.28%). *Bromide salt*: $\delta_P(CDCl_3)$ 22.99; m/z (FAB) 554 ($M^+ - 1$, betaine), 555 (M^+).

2-(4-Triphenylphosphoniophenyl)-1H-phenanthro[9,10-d]-imidazole bromide. Yellow solid, mp 240 °C (decomp.) (Found: C, 73.76; H, 4.50; N, 4.42; $C_{39}H_{28}N_2P \cdot Br$ requires C, 73.71; H, 4.44; N, 4.41%); $\delta_P(CDCl_3)$ 22.53; m/z 555.0 (M^+).

2-(1H-Benzimidazol-2-yl)phenyltributylphosphonium bromide. Off-white solid, characterised as the related *perchlorate*, mp 124–126 °C (Found: C, 60.62; H, 7.34; N, 5.62; $C_{25}H_{36}N_2P \cdot ClO_4$ requires C, 60.66; H, 7.33; N, 5.66%); $\delta_P(-70 °C; CDCl_3)$ 32.23; m/z (FAB) 395.2 base peak (M^+).

3-(1H-Benzimidazol-2-yl)phenyltributylphosphonium bromide. White crystals, mp 180–182 °C (Found: C, 63.05; H, 7.67; N, 5.79; $C_{25}H_{36}N_2PBr$ requires C, 63.16; H, 7.63; N, 5.89%); $\delta_P(-70 °C; CDCl_3)$ 31.82; m/z (FAB) 395.2 base peak (M^+).

4-(1H-Benzimidazol-2-yl)phenyltributylphosphonium bromide. Off-white solid, mp 179–181 °C (Found: C, 62.89; H, 7.67; N, 5.79; $C_{25}H_{36}N_2PBr$ requires C, 63.16; H, 7.63; N, 5.89%); $\delta_P(-70 °C; CDCl_3)$ 30.51; m/z (FAB) 395.0 (M^+).

Phosphonium betaines

Treatment of the phosphonium salts with an equimolar proportion of aqueous sodium hydroxide in ethanol (or methanol depending on the solubility of the salt) led to the formation of the new stable phosphonium betaines which were isolated and characterised.

2-(2-Triphenylphosphoniophenyl)-4,5-diphenylimidazolide. Orange solid, mp >300 °C (decomp., from ethanol–water) (Found: C, 81.52; H, 5.40; N, 4.87; $C_{39}H_{29}N_2P \cdot H_2O$ requires C, 81.51; H, 5.44; N, 4.87%); $\delta_P(CDCl_3)$ 15.60; m/z (FAB) 556.9 ($M^+ + 1$).

2-(4-Triphenylphosphoniophenyl)-4,5-diphenylimidazolide. Orange solid, mp 210 °C (decomp., from ethanol–water) (Found: C, 81.43; H, 5.30; N, 4.78; $C_{39}H_{29}N_2P \cdot H_2O$ requires C, 81.51; H, 5.44; N, 4.87%); $\delta_P(CDCl_3)$ 22.08; m/z (FAB) 556.7 ($M^+ + 1$).

2-(2-Triphenylphosphoniophenyl)-1H-phenanthro[9,10-d]-imidazolide. Orange solid, mp >300 °C (from ethanol–water) (Found: C, 81.82; H, 5.10; N, 4.86; $C_{39}H_{27}N_2P \cdot H_2O$ requires C, 81.80; H, 5.10; N, 4.89%); $\delta_P(CDCl_3)$ 19.87; m/z (FAB) 554.9 base peak ($M^+ + 1$).

2-(4-Triphenylphosphoniophenyl)-1H-phenanthro[9,10-d]-imidazolide. Orange solid, mp 261–263 °C (from ethanol–water) (Found: C, 81.90; H, 5.09; N, 4.85; $C_{39}H_{27}N_2P \cdot H_2O$ requires C, 81.80; H, 5.10; N, 4.89%); $\delta_P(CDCl_3)$ 22.30; m/z (FAB) 555.0 ($M^+ + 1$).

2-(2-Tributylphosphoniophenyl)-1H-benzimidazolide. White solid, mp 133–135 °C (from dichloromethane–diethyl ether) (Found: C, 74.87; H, 6.71; N, 7.0; $C_{25}H_{35}N_2P$ requires C, 76.11; H, 8.94; N, 7.10%); m/z (FAB) 394.1 (M^+).

2-(3-Tributylphosphoniophenyl)-1H-benzimidazolide. White solid, mp 140–143 °C (decomp., from dichloromethane) (Found: C, 70.23; H, 8.94; N, 6.82; $C_{25}H_{35}N_2P \cdot 2H_2O$ requires C, 69.74; H, 9.13; N, 6.51%); $\delta_P(CDCl_3)$ 30.84; m/z (FAB) 395 base peak ($M^+ + 1$).

2-(4-Tributylphosphoniophenyl)-1H-benzimidazolide. Cream solid, mp 278–280 °C (from dichloromethane–diethyl ether) (Found: C, 69.97; H, 8.89; N, 6.50; $C_{25}H_{35}N_2P \cdot 2H_2O$ requires C, 69.74; H, 9.13; N, 6.51%); $\delta_P(CDCl_3)$ 28.96; m/z base peak 394.1 (M^+).

Derivatives of betaines and 4-nitrobenzyl bromide

Refluxing the betaines with an equimolar proportion of 4-nitrobenzyl bromide in either acetonitrile or dimethylformamide resulted in the preparation of the following derivatives which have been characterised.

1-(4-Nitrobenzyl)-2-(4-triphenylphosphoniophenyl)-4,5-diphenylimidazole bromide. Yellow solid, characterised as the related *perchlorate*, mp 164–165 °C (from DMF–diethyl ether) (Found: C, 69.84; H, 4.37; N, 5.15; $C_{46}H_{35}N_3P \cdot ClO_6$ requires C, 69.74; H, 4.38; N, 5.20%).

1-(4-Nitrobenzyl)-2-(2-triphenylphosphoniophenyl)-1H-phenanthro[9,10-d]imidazole bromide. Yellow solid, characterised as the related *perchlorate*, mp 161–163 °C (from DMF–diethyl ether) (Found: C, 69.92; H, 4.22; N, 5.31; $C_{46}H_{33}N_3P \cdot ClO_6$ requires C, 69.92; H, 4.21; N, 5.32%).

1-(4-Nitrobenzyl)-2-(3-triphenylphosphoniophenyl)-1H-phenanthro[9,10-d]imidazole bromide. Yellow solid, characterised as the related *perchlorate*, mp 184–186 °C (from DMF–diethyl ether) (Found: C, 69.84; H, 4.25; N, 5.29; $C_{46}H_{33}N_3P \cdot ClO_6$ requires C, 69.92; H, 4.21; N, 5.32%).

1-(4-Nitrobenzyl)-2-(4-triphenylphosphoniophenyl)-1H-phenanthro[9,10-d]imidazole bromide. Yellow solid, characterised as the related *perchlorate*, mp 188–190 °C (Found: C, 70.01; H, 4.21; N, 5.26; $C_{46}H_{33}N_3P \cdot ClO_6$ requires C, 69.92; H, 4.21; N, 5.32%).

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