Iminophosphorane-substituted Proton Sponges. Part 4. Comparison of X-Ray Molecular Structures with Solution Properties (p*K*a, ^1H and ^{13}C NMR Spectroscopy)

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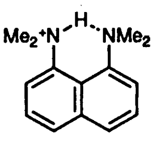
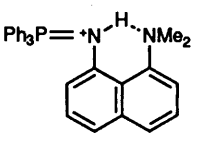
Classical 'proton sponges' related to 1,8-bis(dimethylamino)naphthalene (DMAN) and new ones derived from the replacement of one or both dimethylamino groups by iminophosphorane groups are compared (i) in the solid state using crystallographic data, (ii) in solution in deuteriochloroform and [$^2H_6$]dimethyl sulfoxide by ^1H and ^{13}C NMR spectroscopy, (iii) in water and ethanol–water mixtures by determining their pK_a's. The conclusion is that the new sponges are stronger than the classical ones but, since they decompose when the acid proton is removed are of no practical value as chemical reagents.

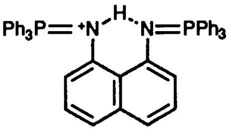
In three preceding papers[1-3] we have described the structure of proton sponges having an iminophosphorane group instead of a dimethylamino one.[4] Here we intend to summarize the information concerning the solid state, to describe the solution properties both in NMR spectroscopy (^1H and ^{13}C) and pK_a, and to draw a general conclusion. The discussion involves compounds **1–11** (the references between brackets indicate where the compounds have been described: Sponges 1,[1] Sponges 2,[2] and Sponges 3,[3] and the numbering of compounds used in those previous papers, for instance compound **4** was compound **1** in Sponges 3).



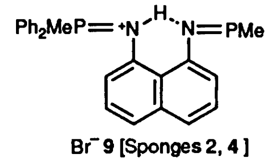
Br^- **1**
BF_4^- **2**
$TeOF_5^-$ **3**



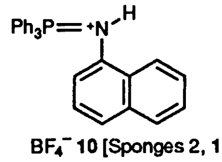
Br^- **4** [Sponges 3, 1]
BF_4^- **5** [Sponges 3, 2]
PF_6^- **6** [Sponges 3, 3]



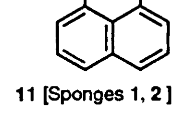
Br^- **7** [Sponges 2, 2]
PF_6^- **8** [Sponges 2, 3]



Br^- **9** [Sponges 2, 4]



BF_4^- **10** [Sponges 2, 1]



11 [Sponges 1, 2]

Results and Discussion

Crystallography.—The crystallographic studies[2,3] carried out on *peri*-naphthalene derivatives where one or both dimethylamino groups of the 'proton sponges'[4] were replaced by iminophosphorane groups leads to the constitution pattern summarized in Fig. 1(*a*). For comparison purposes, this figure also displays the average geometry of 11 salts of 1,8-bis(dimethylamino)naphthalene (DMAN hereinafter).[5-8] The structures[9-11] where the naphthalene moiety is placed on a crystallographic symmetry element were not included in the calculations mentioned but all of them were included in the N···N distance average and range. Fig. 1(*b*) shows the corresponding bond distances and angles of the parent compound, 1,8-diaminonaphthalene,[1] and of naphthalene itself.[12]

The most relevant characteristics of the new 'proton sponges' are: (i) for all the structures, the proton was located unambiguously bound to one iminophosphorane group, regardless of whether the other basic group was an iminophosphorane or a dimethylamino group (proving that the iminophosphorane is more basic than the dimethylamino group). As a consequence of the protonation, a significant lengthening of the N=P double bond occurs, N=P, 1.598(2) Å, N^+=P, 1.612(2) Å. Moreover, a shortening of the N–C_{aryl} bond can also be detected, probably due to some degree of delocalization, when the N=P bond is almost coplanar with the naphthalene plane [C–C–N–P: 1.7(6)–32.6(5)°]. The mean value of the C–N bond length is 1.410(2) Å in contrast to the value of 1.461(12) Å observed[2] when the $-NPPh_3$ group is twisted by $-72.6(12)°$.

(ii) A significant increase of the C–N^+–P angle can be observed when a dimethylamino group acts as acceptor of the intramolecular hydrogen bond (IMHB). However, the C–N^+–P and C–N–P angles are not different in terms of the achieved precision when two iminophosphoranes are present in the cation.

(iii) The opening of the exocyclic C_{ext}–C–N angle for coplanar $-NPPh_3$ groups may be due to steric effects. However, the internal exocyclic angles present a different degree of distortion, C_{int}–C–N^+ < C_{int}–C–N.

The naphthalene ring is also affected by the substituents in such a way that all bond distances involving the fused carbon atom near the substituents (C-8a) and the corresponding exocyclic angles at this position increase their values with respect to 1,8-diaminonaphthalene and to naphthalene itself (see Fig. 1). The ring appears to be less planar when iminophosphorane groups are present. The distortion, measured by the deformation parameters around a bond,[13] displays average χ_T values of 3.5° ranging from 0.2(4) to 5.9(4)° while the corresponding values for DMAN cations are 2.3° and 0.0–

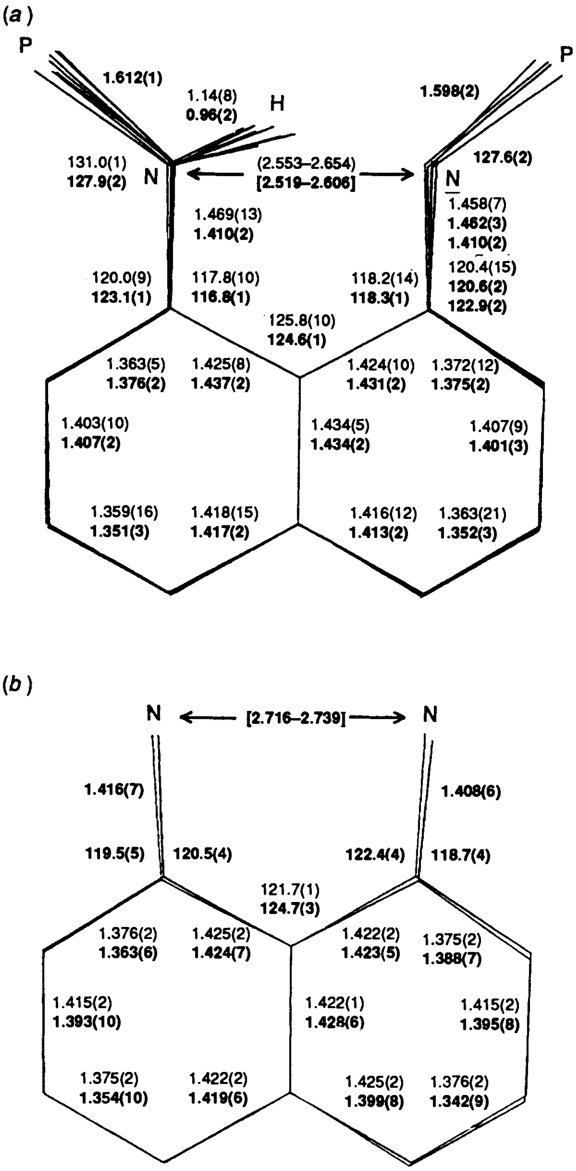


Fig. 1(*a*) Partial superposition of the iminophosphorane derivatives showing the mean bond distances and angles for the 1,8-bis(dimethylamino)naphthalene and the above mentioned compounds (upper and lower values). (*b*) Superposition of the two independent molecules of 1,8-diaminonaphthalene, also displaying the geometry of the naphthalene compound (upper values).

5.2°. All the mentioned distortions result in a shortening of the N···N distance and, consequently, in an increase of the IMHB strength. The corresponding mean values for this series of compounds and for the classical sponges are 2.554(2) and 2.581(1) Å. respectively, both being significantly shorter than that of the parent compound, 2.729(7) Å.

About the influence of the anion, two observations should be made concerning (i) the conformation about the N–P bond and (ii) the correlation between the N···N distance and the size of the anion. The substitution of Br^- or BF_4^- by the PF_6^- anion (compounds **4–6**) modifies either the molecular or the crystal structure. The pseudoisomorphism[3] disappears when the hexafluorophosphate anion is present in the crystal and the parallel conformation about the N–P bond (C–N–P–C *ca.* ±60, 180°)[14] turns perpendicular (±30, ∓150, ±90°) and reciprocally. There is a relationship between the N···N distance and the size of the anion, the shortest distances are always observed in bromide salts: 2.584(4) Å (Br^- **7**) – 2.606(4) Å (PF_6^- **8**) for bis-iminophosphoranes[2] and 2.519(3) (Br^- **4**), 2.543(4) (BF_4^- **5**) and 2.571(6) (PF_6^- **6**) for mixed substituents.[3] We have found a similar situation for DMAN anions **1–3**: 2.554(5) Å for Br^-,[9] 2.562(3) Å for BF_4^-,[6] and 2.574(3)/2.577(4) Å for $TeOF_5^-$.[10,15] All these values can be summarized in an additive model, where DMAN and bromide are taken as reference: N···N bond length = 2.549 + a_1(anion) + a_2(substituents), $n = 10$, $r^2 = 0.94$, with $a_1(BF_4^-) = 0.0132$ Å, $a_1(PF_6^-$ or $TeOF_5^-) = 0.031$ Å, $a_2(Me_2N/N{=}PPh_3) = -0.0193$ Å, $a_2(Ph_3P{=}N/N{=}PPh_3) = 0.0306$ Å and $a_2(Ph_2MeP{=}N/N{=}PMePh_2) = -0.0149$ Å.

All the compounds we have studied have anions that can be considered spherical in shape. The quotients $Q_{ij}^2 = i_{ij}^v/i_{ij}^s$ of the planar inertial moments over the superficial ones,[16] are $Q_{12}^2 = Q_{13}^2 = Q_{23}^2$, 0.61, 0.63, 0.62 in average for Br^-, BF_4^- and PF_6^- anions, values very close to those of a perfect sphere, 0.60, with radii of 1.92, 2.33 and 2.64 Å. respectively.

Table 1 Main geometrical parameters obtained from semiempirical calculations (Å, °)

Compound	Parameter	AM1	PM3
Iminophosphorane proton sponge. Mixed substituents			
4	$N^+{=}P$	1.573	1.751
	$C{-}N^+$	1.414	1.439
	C–C–N–P	82.6	−41.3
6	$N^+{=}P$	1.571	1.739
	$C{-}N^+$	1.404	1.429
	C–C–N–P	−1.4	−18.5
Test molecules			
$H{-}N{=}PH_3$	N–P	1.399	1.628
	H–N–P	180.0	115.6
$H_2N^+{=}PH_3$	N–P	1.529	1.736
	H–N–P	125.5	119.7
$H{-}N{=}CH_2$	N–C	1.270	1.276
	H–N–C	116.6	117.3
$H_2N^+{=}CH_2$	N–C	1.293	1.295
	H–N–C	122.5	121.8

Semiempirical calculations at AM1 and PM3 levels,[17] have been performed to separate the crystal packing effects from the intrinsic conformation of the cations. The two sets of crystallographic coordinates available for the mixed cation (**4–6**) were used as starting points. The most striking aspects of the optimized geometries concern the discrepancies in bond lengths and conformations between both methods, Table 1. While the $N^+{=}P$ value obtained with the PM3 method corresponds to a single bond,[18] that of the AM1 calculation, after performing the bond correction,[19] is close to the experimental value. The C–N bond is insensitive to conformational changes in both methods. To assess the reliability of the preceding results concerning phosphorus derivatives, some additional calculations were carried out on model compounds $H{-}N{=}PH_3$ and $H_2N^+{=}PH_3$. The same discrepancies are observed (Table 1) while a good agreement between both methods is found when the P atom is replaced by a C one ($H{-}N{=}CH_2$ and $H_2N^+{=}CH_2$). In consequence, the phosphorus parametrization of both methods[19,20] is not adequate for such molecules which prevents further exploration of iminophosphorane-substituted proton sponges by semiempirical methods.

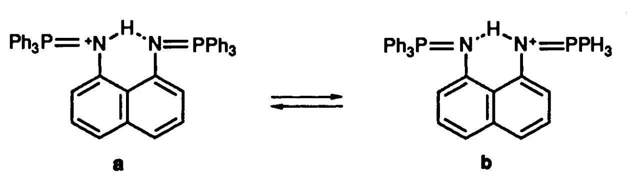
^1H *and* ^{13}C *NMR Spectroscopy*.—The experimental values were described in the experimental part of the preceding papers in this series.[1–3] The most significant data used for the discussion are collected in Table 2.

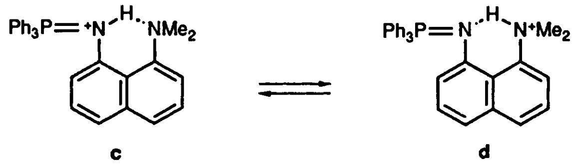
These results correspond to a classical although very rapid tautomeric equilibrium between two forms, **a** and **b**, in the case of bis-iminophosphoranes **7–8** and **c** and **d** in the case of mixed derivatives **4–6** (from now on, the nature of the anion will be

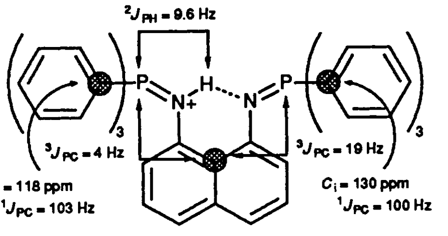
Table 2 Chemical shifts/ppm and coupling constants/Hz of compounds **1–11**

		^1H		^{13}C			
Compound	Solvent	NH	NMe_2	C-1	C-8	C-8a	C_i(Ph)
1–3[4]	[$^2H_6$]DMSO	18.31	2.90				
		^3J 2.0					
	$CDCl_3$	18.30	2.85	145.6	140.2	118.8	122.6
4–6		^3J 2.0		$^4J_{PC}$ 1.4	$^2J_{PC}$ 3.5	$^3J_{PC}$ 11.6	$^1J_{PC}$ 101.3
	[$^2H_6$]DMSO	18.43	2.82	145.8	141.3	118.9	123.1
		^3J 2.0		$^4J_{PC}$ 1.4	$^2J_{PC}$ 3.2	$^3J_{PC}$ 12.3	$^1J_{PC}$ 101.4
7–8	$CDCl_3$	16.42(t)[a]	—	142.6		120.9	123.6
		$^2J_{HP}$ 4.8		J 2.1,2.8[b]		$^3J_{PC}$ 11.6	$^1J_{PC}$ 101.6
9	$CDCl_3$	16.64	2.21[c]	143.0		119.8	124.4
			$^2J_{HP}$ 12.7	J 2.3,2.8[b]		$^3J_{PC}$ 11.8	$^1J_{PC}$ 99.0
10	$CDCl_3$	Not observed	—	124.8	131.9	130.3	120.3
				$^4J_{PC}$ 1.4	$^2J_{PC}$ 3.0	$^3J_{PC}$ 5.3	$^1J_{PC}$ 103.2
11	$CDCl_3$	—	—	148.2	149.4	120.3	130.1
				$^4J_{PC}$ 1.5	$^2J_{PC}$ 3.1	$^3J_{PC}$ 20.6	$^1J_{PC}$ 100.0

[a] In [$^2H_6$]DMSO the signal appears as a triplet, δ 16.47, $^2J_{HP}$ 4.8. [b] The real coupling constants are: $^2J_{PC}$ 3.52, $^4J_{PC}$ 1.35 and $^4J_{PP}$ *ca.* 3 (compound **7**, see text). [c] This value corresponds to a $^{31}P–CH_3$ coupling.







a

neglected). The fact that these equilibria are very fast, as in DMAN derivatives,[4] is shown by the narrow appearance of the averaged signals.

Assuming that the ^3J(H–C–N$^+$–H) coupling of the methyl groups in the absence of prototropy is 4.0 Hz (methylaniline in trifluoroacetic acid shows its methyl group as a triplet with a $^3J = 5.5$ Hz)[21] and that in tautomer **a** the following couplings are present, all the data of Table 2 are consistent with a 50:50 mixture of tautomers **a** and **b** (by definition $K_T = 1$) and a 58($\pm$2):42($\pm$2) mixture of tautomers **c** and **d**.

The NH signal, very characteristic of 'Proton Sponges',[4,22] appears at about 18.3 ppm both in **1–3** and in **4–6**. When both dimethylamino groups are removed, **7–9**, the NH is shifted upfield to 16.5 ppm. This shift could be related to anisotropic effects of the triphenylphosphine groups.

Another interesting aspect of the spectra of compounds **7–9** is the appearance of the signal belonging to carbons C-1 and C-8. Due to the rapid prototropy they appear as a single quartet with apparent coupling constants with both phosphorus atoms of 2.2 and 2.8 Hz. In fact, the quartet has an abnormal aspect with the external transitions being twice as intense as the central ones. An iterative analysis of the AA′ part (carbons C-1 and C-8) of an AA′XX′ system (compound **7**) yields a simulated ^{13}C NMR pattern identical to the experimental with $^2J_{PC} = 3.52$, $^4J_{PC} = 1.35$ and $^4J_{PP}$ *ca.* 3 Hz (the spectrum is rather insensitive to small variations of this coupling constant). We prefer a ^4J(P=N$^+$–H$\cdots$N=P) to a ^6J(P=N$^+$C–C–C–C–N=P) pathway. The calculated $^{31}P–^{13}C$ coupling constants are in good agreement with those of model compounds **10** (a salt) and **11** (a neutral derivative) being independent of the charge on the nitrogen atom.

Basicity Measurements.—Our intention was to determine the thermodynamic, *i.e.* in water at 25 °C, pK_a of the 1,8-bis(iminophosphorane)naphthalene (BIPN) and compare it with that of the standard 'proton sponge' DMAN. A survey of the literature concerning superbases shows that almost no thermodynamic values have been found. In some cases, an approximate value is obtained by competition experiments monitored by NMR spectroscopy,[22–24] in others, non-protic solvents were used (dioxane,[25] THF,[26,27] acetonitrile,[27–29] DMSO,[4,30] *etc.*). We failed to obtain this value experimentally for two reasons: (i) the iminotriphenylphosphorane derivatives are very insoluble in water; (ii) as with conventional 'proton sponges'[31] the kinetic acidity is very low and 'slow' determinations are necessary which results in decomposition (hydrolysis) of the iminophosphorane into triphenylphosphine oxide and free amine. It is not possible to obtain free BIPN from salts **7** or **8**,[2,3] since the compound decomposes and thus, all the measurements are backward titrations from the salts.

To estimate the thermodynamic basicity of BIPN, we have decomposed its basicity into three contributions: (i) the solvent (76% ethanol–water *vs.* water), (ii) the basic centre (NMe_2 *vs.* N=PPh_3) and (iii) the presence of an intramolecular hydrogen bond (none *vs.* one IMHB). We have represented the eight possibilities (see Fig. 2) as a classical 2^3 factorial design.[32]

The lower face corresponds to 76% ethanol–water (25 °C) and the upper one to pure water (25 °C), the right side corresponds to iminophosphoranes and the left one to dimethylamino derivatives, and finally, the front face corresponds to the presence of an IMHB and the back one to its absence. In summary: variable 1, level (−), 76% ethanol, level (+), H_2O; variable 2, level (−), NMe_2, level (+), N=PPh_3; variable 3, level (−), without IMHB, level (+), with IMHB. The eight vertices correspond to:

(1) pK_a of *N*,*N*-dimethylaniline in 76% ethanol–water at

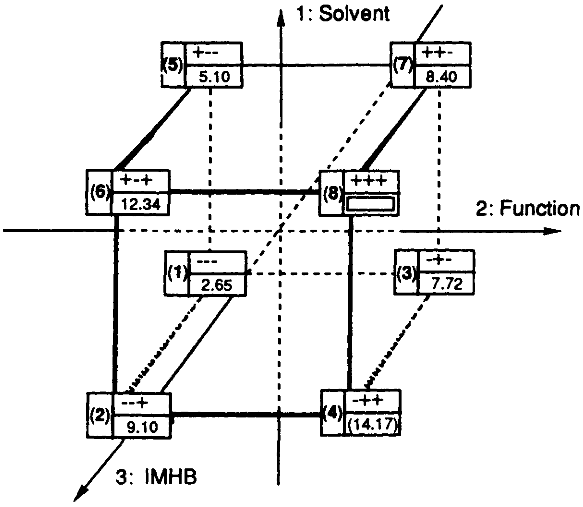


Fig. 2 2^3 factorial representation of 'Proton Sponges' basicity

25 °C. Estimated by linear interpolation of mixtures of ethanol and water at 25 °C.[33] pK_a = 5.10 − 0.0322 (% ethanol), n = 10, R = 0.99; for 76% ethanol, pK_a = 2.65.

(**2**) pK_a of DMAN in 76% ethanol–water at 25 °C = 9.10 ± 0.02 (determined by potentiometry).

(**3**) pK_a of *N*-phenyliminotriphenylphosphorane, Ph–N=PPh$_3$, in 76% ethanol–water at 25 °C. This value has been determined by potentiometry to be 7.72 ± 0.01. In 10% ethanol the value (determined spectrophotometrically at 257, 262 and 275 nm) is 8.40 ± 0.06, identical to that found in pure water. The pK_a of salt **10**, naphthyl-N=PPh$_3$, has been determined in 76% ethanol–water at 25 °C both by potentiometry (6.81 ± 0.02) and by spectrophotometry (at 246 and 333 nm, 6.78 ± 0.04) proving the reliability of the experimental methodology. The base-weakening effect from benzene to 1-naphthalene (0.91 pK_a units) is parallel to the effect observed for *N*,*N*-dimethylamino derivatives.[33] The pK_a of the free base **11** determined spectrophotometrically in 76% ethanol (analytical wavelengths = 252 and 353 nm) is 6.77 ± 0.03. The pK_a corresponding to salts **4**–**6** can be determined neither by potentiometry nor by spectrophotometry. Only a lower limit of pK_a > 11 can be obtained (analytical wavelengths: 266, 273 and 355 nm).

(**4**) pK_a of BIPN in 76% ethanol–water at 25 °C. Only a lower limit of 13.65 for the pK_a can be obtained (analytical wavelengths: 266, 272 and 354 nm). Assuming that the increase of basicity between (**1**) and (**3**) (+5.07 pK_a units) is the same as for the pair (**2**)–(**4**), then the last value should be 14.17. This assumption corresponds to the hypothesis that there is no interaction between variables 2 and 3 (a_{23} = 0, see below).

(**5**) pK_a of *N*,*N*-dimethylaniline in water at 25 °C = 5.10.[33]

(**6**) pK_a of DMAN in water at 25 °C = 12.1.[4,25,26]

(**7**) pK_a of Ph–N=PPh$_3$ in water at 25 °C = 8.40 ± 0.04 (spectrophotometrical determination at 255 and 277 nm). The pK_a of this compound in nitromethane is 16.74,[34] which, taking into account the value for *N*,*N*-dimethylaniline in the same solvent (11.00), corresponds to the relationship pK_a(CH$_3$NO$_2$) = 2.13 + 1.74 pK_a(H$_2$O).

(**8**) This vertex corresponds to the value to be estimated, *i.e.* the pK_a of BIPN in water at 25 °C. For this estimation we postulated that pK_a **8** = $a_0 + a_1x_1 + a_2x_2 + a_3x_3 + a_{12}x_1x_2 + a_{13}x_1x_3$, where x_i can take the values 0 (− level) or 1 (+ level). A multiple regression (seven values, six coefficients) yields (*R ca.* 1): a_0 = 2.65 (pK_a of **1**), a_1 = 2.45, a_2 = 5.07, a_3 = 6.45, a_{12} = −1.77, a_{13} = 0.79 (all these coefficients are in pK_a units) and the estimated pK_a **8** = 15.64.

The largest principal effects are those due to the function x_2 and to the IMHB x_3. The interaction terms are less important, but there is a negative interaction between the solvent and the function x_{12} which corresponds to the interaction between water and iminophosphoranes.

Conclusions

We have found three different situations for iminophosphorane-substituted proton sponges. (i) In the solid state they are stronger than classical sponges since their IMHB are stronger; moreover, in the case of salts **4**–**6**, the proton prefers the iminophosphorane to the dimethylamino group. (ii) In solution, CDCl$_3$ and DMSO, both kinds of sponges are either similar (according to the chemical shift of the N–H proton and to the position of the equilibrium between cations **c** and **d**) or the protonation on the iminophosphorane is slightly preferred. (iii) Finally, the estimated thermodynamic pK_a of BIPN is 3.54 pK_a units more basic than that of DMAN, but this estimation strongly relies on the value for situation **4** (Fig. 2). Overall, the new sponges are stronger than the classical ones but are of no practical value since the free bases cannot be prepared.

Experimental

All compounds have been described in previous papers.[1–3]

Determination of the pK_a*'s.* General conditions: 76% ethanol–water solution, unless otherwise indicated. Ionic strength, 0.1 mol dm^{-3}, KCl. Potentiometric determinations were performed with a Radiometer Titralab™ VIT90 titration system with a thermostatted cell (25.0 ± 0.1 °C). All titrations were carried out under nitrogen atmosphere, with 0.1 mol dm^{-3} NaOH as titrating solution. The equipment was calibrated against standard aqueous solutions (±0.01 pH units). The experimental pH values measured in 76% ethanol–water were transformed into activities following Bates *et al.*[35] Spectrophotometric pK_a values were determined according to the method described by Ernst and Menashi.[36] A Cary 210 spectrophotometer fitted with a thermostatted (25.0 ± 0.1 °C) cell compartment was used. An electrode type GK2401B from Radiometer was employed for pH measurements above 12.0. The spectra of each compound were recorded at different pHs and pK_a values were calculated from data at those wavelengths (analytical wavelength) where the variations were maximum. In each case, it was checked that variations in absorbance corresponded to a simple equilibrium. In the experiments corresponding to salts **4**–**6** the lower limit was the pH value where the UV spectrum does not show any modification. At stronger basic conditions, a slow irreversible change in the spectrum was observed. In the case of salts **7**–**8** variations in the spectrum were observed in the pH range of 13.0–14.0, although above pH = 13.5 spectral changes associated with the irreversible modification of the spectrum became evident. Therefore, only a lower limit for the pK_a value of 13.65 could be estimated (several anions were used without any difference including the solubility problems).

^{1}H and ^{13}C NMR spectra were measured with a Bruker AC-200 spectrometer (SiMe$_4$ internal reference; all chemical shifts are expressed as δ values and coupling constants in Hz).

Acknowledgements

Dr. M. L. Jimeno's help in analysing the ^{13}C NMR spectra of compound **7** is greatly acknowledged. We thank the CICYT of Spain for financial support (PB90-0070).

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Paper 2/05730A
Received 27*th October* 1992
Accepted 10*th December* 1992