SHORT PAPER

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Synthesis of a solvatochromic triphenylphosphonium-*p*-toluenesulfonaminido betaine†

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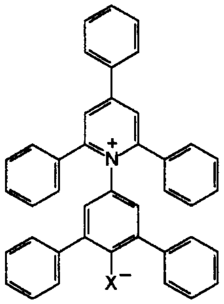
The synthesis, crystal structure, and negative solvatochromism of the triphenylphosphonium-*p*-toluenesulfonaminido betaine (**4**) are described.

The pyridinium -phenolate betaine (**1**, X = O) (Reichardt's dye) is well-known for its negative solvatochromic behaviour in solvents of increasing polarity, and for the wide range of solvatochromic shifts exhibited.[1-3] There has been interest in the synthesis of related systems in which the phenolate oxygen has been replaced by other electron-rich centres, such as sulfur (1, X = S)[4], dicyanomethanide (X = C(CN)$_2$)[5], and nitrogen , as in the sulfonaminido system (**2**)[6].



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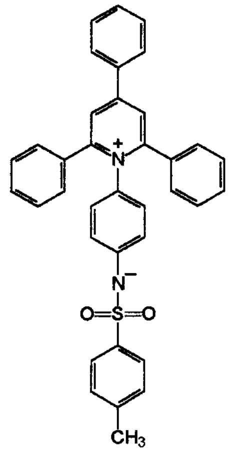

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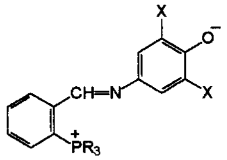
In recent work, we have investigated the effects of variation at the cationic centre in such dipolar species, and have described a series of phosphonium, arsonium, and stibonium iminophenolate and related azophenolate betaines, e.g., (**3**, X = Cl, Br, Ph, or Bu^t), all of which show significant negative solvatochromic behaviour.[7,8] Currently, there is increasing interest in the optical properties of organic derivatives of the main group 15 elements.[9,10] We now describe the synthesis and solvatochromism of the phosphonium sulfonaminido betaine (**4**), so as to enable a comparison with the pyridinium system (**2**).



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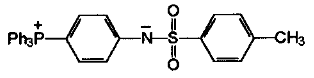

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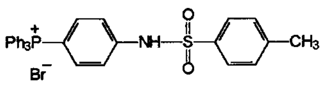

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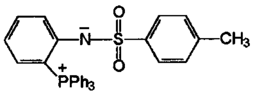

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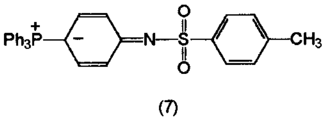
The route to the phosphonio-sulfonaminido betaine (**4**) involved the Horner[11] reaction of the N-tosyl derivative of *p*-bromoaniline with triphenylphosphine in the presence of nickel(II) bromide, in refluxing benzonitrile, giving the intermediate phosphonium salt (**5**), (δ^{31}P (in DMSO) = 21.9ppm) as a white solid. Treatment of the salt in ethanol with an excess of aqueous sodium hydroxide solution resulted in crystallisation of the betaine (**4**) as a very pale yellow solid, (δ^{31}P (in DDMSO) = 21.2ppm), which gave a negative response when tested for the presence of halide ions with acidified silver nitrate. Comparison of the ^{1}H NMR spectra of the salt and betaine in DDMSO showed that whereas in the salt, the aromatic protons appeared in the range 7.3–8.1 ppm, those of the betaine appeared at 6.9–7.9 ppm, indicating slight shielding by the negative charge. The betaine was found to be sparingly soluble in dichloromethane, acetonitrile, ethanol and methanol, and relatively easily soluble in dimethylsulfoxide and dimethylformamide, indicating its very polar nature. Both salt and betaine gave a molecular ion at *m/z* 507.1 under FABMS conditions, as expected, the betaine being protonated under these conditions to give the same phosphonium cation displayed by the salt. The structure of the betaine was confirmed by X-ray crystallography (see below). Attempts to prepare the related *o*-phosphoniophenyl sulfonaminido betaine (**6**) by the same approach were unsuccessful, the *p*-tosyl derivative of *o*-bromoaniline failing to undergo the Horner reaction with triphenylphosphine.

Comparison of the UV-visible absorption spectra of the salt (**5**) and betaine (**4**) in a limited range of solvents (methanol, dichloromethane, and THF) revealed that whereas the absorption maximum of the salt remained essentially constant in the range 270–276 nm, that of the betaine occurred at significantly longer wavelength, (318 nm (methanol), 320 nm (isopropanol), 330 nm (dichloromethane), 332nm (DMF), 336 nm(pyridine) and 335 nm (THF)). The movement of the absorption maximum to longer wavelength as the polarity of the solvent decreases indicates that the betaine displays a limited degree of negative solvatochromism, reflecting the stabilisation in the more polar solvents of the ground state dipolar form relative to less polar excited states, e.g. (**7**). The wavelength of absorption and the degree of solvatochromism of the phosphonium betaine (**4**) are considerably smaller than those of the pyridinium system (**2**), which shows maxima 423



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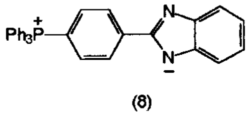

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† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 1. Selected bond lengths (Å) and angles (º) for (**4**).

P(1)–C(11)	1.772(6)	P(1)–C(20)	1.7921(6)
P(1)–C(26)	1.795(6)	P(1)–C(14)	1.798(6)
S(1)–O(1)	1.450(4)	S(1)–O(2)	1.440(3)
S(1)–C(5)	1.775(7)	S(1)–N(1)	1.584(5)
N(1)–C(8)	1.365(2)		
C(11)–P(1)–C(20)	110.17(7)	C(11)–P(1)–C(26)	109.18(7)
C(20)–P(1)–C(26)	109.69(8)	C(11)–P(1)–C(14)	110.47(7)
C(20)–P(1)–C(14)	107.59(7)	C(26)–P(1)–C(14)	109.72(8)
O(1)–S(1)–O(2)	115.40(8)	O(2)–S(1)–N(1)	106.77(8)
O(1)–S(1)–N(1)	114.94(8)	O(2)–S(1)–C(5)	105.98(8)
O(1)–S(1)–C(5)	106.31(8)	N(1)–S(1)–C(5)	106.78(8)
C(8)–N(1)–S(1)	122.02(12)		

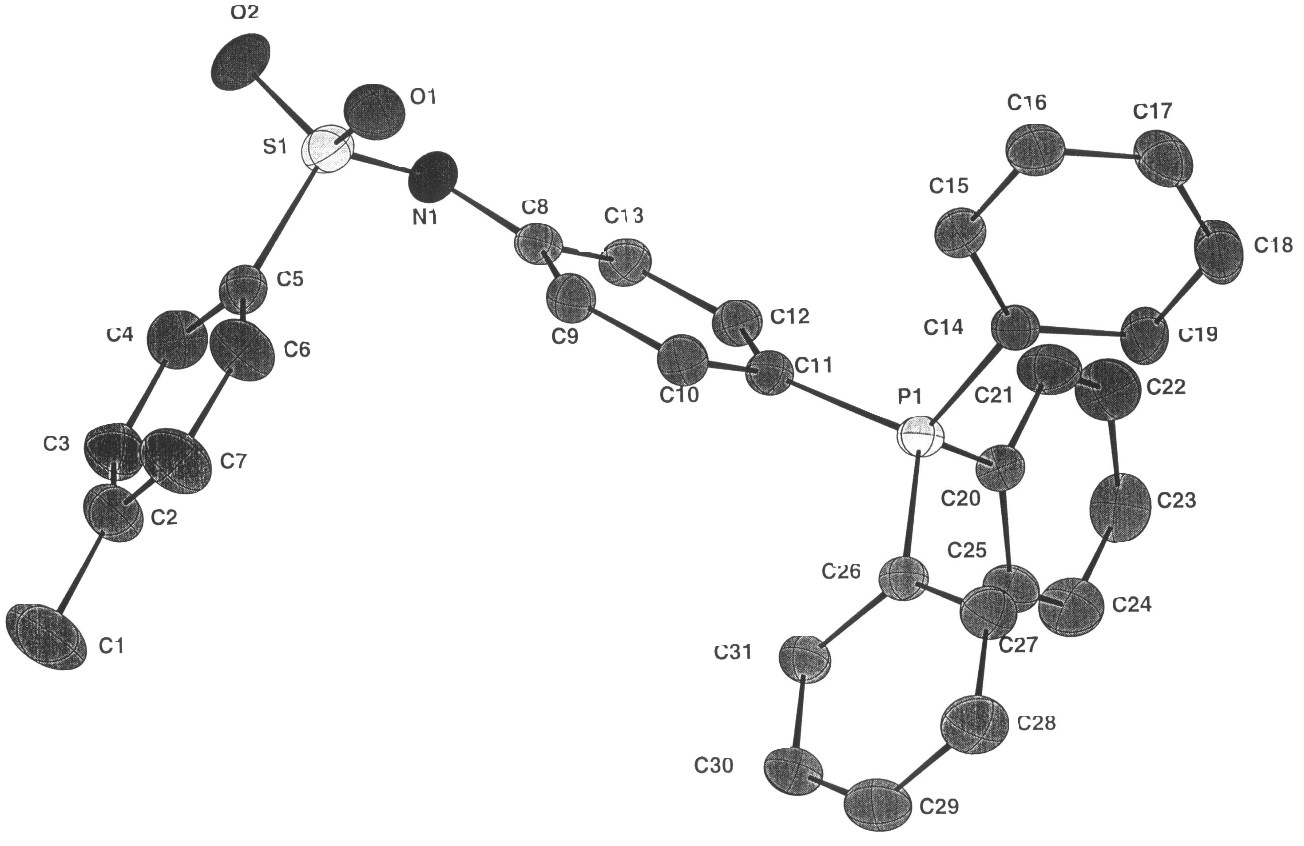
and 512 nm in methanol and dichloromethane, respectively, no doubt reflecting the much smaller ability of the phosphonium group to assist in the delocalisation of the negative charge as a result of its now recognised reluctance to be involved in d_π-bonding.[12] The solvatochromism of the betaine (**4**) is also reduced compared to the phosphonium benzimidazolide (**8**), which shows maxima of 330 and 394 nm in methanol and dichloromethane, respectively[13], indicating that the negative charge is more localised on the sulfonaminido unit than it is on the heterocyclic system in the latter.

Crystal structure of the betaine (**4**): Suitable crystals were obtained by recrystallisation from methanol. The molecular structure is shown in Figure 1 and selected bond lengths and angles are presented in Table 1. A comparison of bond lengths and angles in the sulfonaminido unit in (**4**) with the related parameters for the pyridinium sulfonaminide (**2**)[6] reveals great similarity. The torsion angles used to describe the conformation of the sulfonaminide group in the crystal structure report of (**2**) are very similar to those in (**4**), with (**2**) exhibiting a slightly greater degree of twisting of the group about the S atom. This is due to an intramolecular hydrogen bond (C9–H9···O1) forming a virtual six-membered ring that is present in both structures but stronger in (**2**) [H···O = 2.444(2), 2.23(4)Å and C–H···O = 118.97(11), 128.0(3)° for (**4**) and (**2**) respectively]. This non-bonded interaction causes the main difference in conformation between the two sulfonaminides, the orientation of the sulfonaminide group with respect to its substituent [S1–N1–C8–C9 = 0.93(3), 26.2(7)° for (**4**) and (**2**) respectively]. A decrease in the endocyclic angle at C8 from 120 to116.18(14)°, typical for this electron withdrawing substituent, is observed. In addition an increase in the angle about C9 from 120 to 121.19(15)° results from the influence of the *p*-toluenesulfonyl substituent at the aminide N1 atom. The sp^2 hybridisation of N1 is demonstrated by the contraction of the C8–N1 and N1–S1 bond lengths [1.365(2) and 1.584(5)Å] and the C8–N1–S1 angle being close to 120º [122.02(12)º]. This is further highlighted by comparing bond lengths and angles around N1 with those of the equivalent nitrogen atom in previously determined structures[14] containing secondary amines in the *p*-toluene sulfonamide unit [C8–N1 = 1.365(2), 1.426(3)Å; N1–S1 = 1.584(5), 1.629(3)Å; C8–N1–S1 = 22.02(12), 124.36(9)º for (**4**) and averaged values for three –NH– structures respectively]. The smaller values obtained for the geometric parameters about the aminide nitrogen, when compared with a secondary amine in the same environment, suggest a greater degree of sp^2 hybridisation.

The packing of (**4**) arises from a hydrogen bond between O2 and an aromatic carbon in the PPh_3 group [O2···H22–C22 = 3.198(3)Å], forming a 'head to tail' dimer, which in turn forms sheets through weak π-π aromatic interactions. Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC), see 'Instructions for authors, *J. Chem. Res*., 1999, issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 9/07319A/J.

Experimental

^{31}P and ^{1}H NMR studies were carried out using a Bruker AC250 FTNMR spectrometer. Accurate FAB mass spectrometry measurements were carried out at the EPSRC National Mass Spectrometry Service Centre, University of Wales, Swansea.



*4-N- (p-Toluenesulfonamido)phenyl-1-triphenylphosphonium bromide (**5**):* Triphenylphosphine, (2.53 g, 9.7 mmol), 1-bromo-4-N-(p-toluenesulfonamido)benzene, (3.14 g, 9.6 mmole), and nickel(II) bromide (1.1 g, 5 mmol), were heated together under reflux in benzonitrile (20cm^3) under nitrogen for 4 h. The resulting deep green solution was then poured into aqueous potassium bromide solution (10%w/v, 100 cm^3), and the mixture extracted with dichloromethane (2× 100 cm^3). The combined extracts were dried ($MgSO_4$), and evaporated to give an oily residue which, on repeated trituration with diethyl ether, gave the phosphonium salt as a white solid, (2.62 g, 46%), mp 254–256°C. δ^1H($CDCl_3$): 2.3 (3H,s, CH_3), 11.3 (1H,s,NH, exhanges with D_2O), 7.1–8.0 (23H, br m, ArH) ppm; δ^1H(DDMSO): 2.4(3H,s,CH_3), 7.3–8.1 (23H, br m,ArH),11.4 (1H, br s, NH, exchanges with D_2O) ppm. δ^{31}P(DDMSO): 21.9 ppm. M^+ (FABMS): Found 508.1503 (cation) (–0.5ppm); $C_{31}H_{27}NO_2PS$ requires M^+ = 508.1500.

*1-Triphenylphosphoniophenyl-4-N-(p-toluenesulfonaminido) benzene (**4**):* The phosphonium salt (**5**) was dissolved in ethanol and treated with aqueous sodium hydroxide solution (0.1 mol l^{-1}, 3 mol equiv), causing the betaine (**4**) to crystallise as a very pale yellow solid, in quantitative yield, m.p. >350°C. δ^1H (DDMSO): 2.3 (3H,s,CH_3), and 6.9–7.9 (23H, br m,ArH). δ^{31}P(DDMSO): 21.2ppm. M^+ (FABMS): Found 508.1509 (M+1) (-1.7ppm); $C_{31}H_{27}NO_2PS$ requires M^+ = 508.1500.

Crystal data: $C_{31}H_{26}NO_2PS$, M_r = 507.56, Triclinic space group, a = 9.379(2), b = 11.373(2), c = 12.896(3)Å, α = 86.73(3), β = 71.42(3), γ = 82.39(3)°, U = 1292.2(5)Å^3, Z = 2, D_c = 1.304g cm^{-3}, μ = 0.217mm^{-1}, F(000) = 532, crystal size 0.25 × 0.25 × 0.17mm. Data were collected at 293K, on a Nonius KappaCCD area detector diffractometer[15], at the window of a Nonius FR591 rotating anode (λ Mo-kα = 0.71073Å). Combined φ and ω scans, with a frame increment of 2.0°, gave 99.6% completeness to θ_{max} = 27.49° (index ranges $-12 \le h \le 12$, $-14 \le k \le 14$, $-16 \le l \le 16$). A correction was applied to account for absorption effects by means of comparing equivalent reflections, using the program SORTAV[16] (transmission factors = 0.925 / 0.965). A solution was obtained *via* direct methods and refined[17] by full-matrix least-squares on F^2, with hydrogens included in idealised positions. 5906 unique data were produced from 41131 measured reflections (R_{int} = 0.0456). 326 parameters refined to R_1 = 0.0453 and wR_2 = 0.1340 [I>2σ(I)] (R_1 = 0.0612 and wR_2 = 0.1469 for all data), with residual electron densities of 0.287 and –0.323eÅ^{-3}.

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